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Characterization of Explosives Contamination at Military Firing Ranges

Thomas F. Jenkins, Judith C. Pennington, Thomas A. Ranney,
Thomas E. Berry Jr., Paul H. Miyares, Marianne E. Walsh,
Alan D. Hewitt, Nancy M. Perron, Louise V. Parker, Charlotte A. Hayes,
and Eric G. Wahlgren

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month. Other isomers of DNT, 2,4,6-TNT, and two environmental transformation products of 2,4-DNT (2ANT and 4ANT) were also detected at much lower concentrations.

Soil samples were also collected from a number of areas around detonation craters formed by 105-mm and 155-m howitzers, and 60-, 81- and 120-mm mortars. Concentrations of explosives residues in and around these craters were generally barely detectable, indicating that only minor amounts of explosives residue are deposited during high-order detonations of army munitions.

Soil samples were also collected below and adjacent to a 155-mm howitzer shell that had undergone a low-order detonation. These samples were heavily contaminated with TNT and its environmental transformation products. These results indicate that efforts should be made to find and remove the resulting debris from low-order detonations whenever possible to prevent leaching of contaminants to groundwater.

Water samples collected from five groundwater monitoring wells and five seeps around the artillery impact areas at Fort Lewis were also analyzed for explosives; 8 of the 10 were found to contain very low (<1.0 µg/L) concentrations of RDX. The source of this RDX is unknown.

Cover: Detonations of 105-mm howitzer rounds at Central Impact Area, Fort Lewis.

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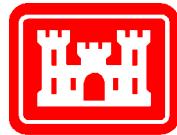
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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Engineer Research and Development Center (ERDC), Hanover, New Hampshire; Dr. Judith C. Pennington, Research Biologist, Environmental Sensing Branch, Environmental Laboratory, ERDC, Vicksburg, Mississippi; Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, New Hampshire; Thomas E. Berry Jr., Research Physical Sciences Technician, Environmental Sensing Branch, Environmental Laboratory, ERDC, Vicksburg, Mississippi; Dr. Paul H. Miyares, Research Chemist, formerly of CRREL; Marianne E. Walsh, Research Chemical Engineer, and Alan D. Hewitt, Research Physical Scientist, Environmental Sciences Branch, CRREL; Nancy M. Perron, Physical Sciences Technician, Snow and Ice Branch, CRREL; Louise V. Parker, Research Physical Scientist, Applied and Military Engineering Branch, CRREL; Charlotte A. Hayes, Staff Scientist, DynTel, Reston, Virginia; and Major Eric G. Wahlgren, former Commander of CRREL's Alaska Projects Office, Fairbanks, Alaska.

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NOMENCLATURE

AcN	Acetonitrile	RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
ADNTs	Aminodinitrotoluenes	RP-HPLC-UV	Reversed-phase high-performance liquid chromatography ultraviolet detection
CFAD	Canadian Force Ammunition Depot	SARM	Standard Analytical Reference Materials
CHPPM	Center for Health Promotion and Preventive Medicine	TNB	1,3,5-trinitrobenzene
CRREL	Cold Regions Research and Engineering Laboratory	TNT	2,4,6-trinitrotoluene
DO	Dissolved oxygen	UXO	Unexploded ordnance
DODIC	Department of Defense Information Code	USARAK	U.S. Army Alaska
EL	Environmental Laboratory	USARPAC	U.S. Army Pacific Command
EOD	Explosive ordnance disposal	WES	Waterways Experiment Station
EPA	Environmental Protection Agency	2-ADNT	2-amino-4,6-dinitrotoluene
ERDC	Engineer Research and Development Center	4-ADNT	4-amino-2,6-dinitrotoluene
GC-ECD	Gas chromatography-electron capture detection	2A4NT	2-amino-4-nitrotoluene
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	4A2NT	4-amino-2-nitrotoluene
LAW	Light Antitank Weapon	3,5-DNA	3,5-dinitroaniline
MMR	Massachusetts Military Reservation	1,3-DNB	1,3-dinitrobenzene
		2,4-DNT	2,4-dinitrotoluene
		2,4,6-TNT	2,4,6-trinitrotoluene
		3-NA	3-nitroaniline

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INTRODUCTION

Testing and training ranges are essential elements to maintaining readiness for the Armed Forces of the United States. Recently, though, concerns have increased over potential environmental effects from testing and training activities at impact ranges within these facilities. In particular, an ongoing investigation at the Massachusetts Military Reservation (MMR) has indicated that the underlying groundwater aquifer below this site is contaminated with low concentrations of RDX (EPA 2000a). The source of this RDX is uncertain, but it may be related to activities on MMR's impact ranges.

Previous research at Canadian Force Base Valcartier (Jenkins et al. 1997, Thiboutot et al. 1998), and at Fort Ord (Jenkins et al. 1998) have indicated that explosives residues are deposited on the surface soils at antitank ranges because of the high usage of LAW rockets at these sites. The main charge in the LAW rockets is octol, which is 60/40 HMX/TNT. Concentrations of HMX accumulated near tank targets at concentrations as high as 1,640,000 µg/kg in surface soils at Valcartier, and as high as 587,000 µg/kg in surface soils at Fort Ord. TNT, however, was found at concentrations only about one-hundredth that of HMX at both sites.

Several other investigations have been conducted in Canada on range contamination with explosives. In addition to the Valcartier range, Thiboutot et al. (1998) sampled four other antitank ranges, two at Western Area Training Center Wainwright and two at Canadian Force Ammunition Depot (CFAD) Dundurn. The results were similar to those reported for Valcartier: relatively high levels of HMX in surface soils, but much lower concentrations of TNT. The highest concentration of HMX

detected at these ranges was 3,700,000 µg/kg at Range 13 at Wainwright. HMX concentrations were much lower at the other ranges due to a much lower usage of these ranges.

In another study, Thiboutot and Ampleman (2000) collected 87 composite soil samples at Canadian Force Training Range Tracadie in New Brunswick. The range sampled had been used for artillery, gun, and mortar firing and was heavily contaminated with unexploded ordnance (UXO). Nevertheless, no explosives residues were detected by RP-HPLC analysis (EPA 1994).

Similarly, Ampleman et al. (2000) collected soil samples at several ranges at Canadian Force Base Chilliwack in British Columbia. Areas of the Slesse Range were used for cratering, and another area for concrete, steel, and wood cutting. Low ppm concentrations of TNT and RDX were found in both areas. The Vokes grenade range was sampled and low ppm levels of RDX and HMX were found. Visual characterization at a propellant burning area at CFAD Rocky Point, however, indicated that the site was littered with partially burned propellant grains. Propellant grains all contain nitrocellulose, and some contain nitroglycerin and nitroguanidine, as well.

Recently the U.S. Army CHPPM conducted a study at the artillery impact area at Camp Shelby, Mississippi (USACHPPM, in press). In this study a large number of surface soil samples was collected in a grid pattern over a large area at the Camp Shelby site. Analysis of soil samples indicated that there was very little detectable residue of explosives-related contaminants at this range. However, soil samples were characterized using RP-HPLC Method 8330, which has detection limits of about 250 µg/kg.

The overall project, of which this is a part, was designed to develop techniques for assessing the potential for environmental impacts from energetic materials on testing and training ranges. Techniques are being developed to define the physical and chemical properties, concentration, and distribution of energetics and residues of energetics in soils, estimate the concentrations of various energetic materials that are deposited from high-order detonations of various military munitions, and assess the potential for transport of these materials to groundwater. Other issues, such as off-site transport in surface runoff, or as a component of airborne dust, are also important, but are beyond the scope of the project.

The study will be executed in two parts: range characterization, and fate and transport parameters for explosives residues. To characterize ranges, heavy artillery impact and firing points, and hand grenade ranges will be sampled. Where possible, groundwater associated with the ranges will also be sampled. Chemical residues from live fire or demolitions of specific rounds will be assessed by detonations on snow cover. To fill data gaps in transport parameters, such as dissolution kinetics and partitioning coefficients, laboratory scale batch tests will be conducted.

OBJECTIVES

The major objective of the research reported here was to determine the magnitude and variability of explosives residues in surface soils resulting from training activities at several types of training ranges at major U.S. Army training facilities. It is hoped that this type of information will help assess the potential for contamination of groundwater with explosives-related contaminants. A long-term objective of this work includes the development of a protocol that can be used to determine the nature and extent of surface soil contamination around impact areas that will include the sampling strategy and analytical methods best suited to this application. Data generated with this protocol can then be used to estimate a source term for post-blast residues based upon the extent of surface soil contamination at a specific site. To address these objectives, ranges were sampled at Fort Lewis, Washington, and at Fort Richardson, Alaska. At Fort Lewis, we investigated surface contamination at two types of ranges: an artillery range and a hand grenade range. On the artillery range, we sampled in front of a 105-mm howitzer firing position, and in the main impact area. In the hand grenade range, we selected one of the four test ranges and sampled surface soils and soils collected at several shallow depths in the subsoil. We also analyzed a set of groundwater samples collected from monitoring wells and

seeps. At Fort Richardson, we sampled a hand grenade range to determine whether the results would be consistent with those obtained for the Fort Lewis grenade range.

SITE DESCRIPTION, SOIL AND GROUNDWATER SAMPLING, FORT LEWIS, WASHINGTON

Fort Lewis is located approximately 10 miles west of Olympia, Washington, and adjacent to McChord Air Force Base. Fort Lewis, part of Forces Command, is the home of First Corps, one of 15 U.S. power projection platforms. The Corps' primary focus is Pacific Rim. Fort Lewis includes 115 live fire ranges and encompasses 86,000 acres. Soil sampling was conducted at Fort Lewis, Washington, on 7 and 8 July 2000. Three distinct functional areas at Fort Lewis were chosen for soil sampling. The three areas sampled were a hand grenade range impact area, a firing point for artillery, and an artillery impact area.

Hand grenade range

The grenade range at Fort Lewis is divided into four separate launching and impact areas separated by concrete and wooden walls and has been actively used for at least 30 years.* It is estimated that about 6,000 to 7,000 grenades are thrown on the range each year, or about 1,500 to 1,750 grenades per launching area per year.

Currently about 95% of the hand grenades detonated on this range are M67 fragmentation grenades, which are the type of hand grenade currently used by the U.S. Army. The other 5% of the grenades used at this range are of Canadian and British manufacture and used by Canadian and British troops who train regularly at Fort Lewis. The Canadian hand grenade is model C7, but is manufactured to the same specification as the U.S. M67. The current British hand grenade is the Model L2, which is based on the older U.S. M26 hand grenade.

The M67 and C7 grenades contain 186 g of Composition B as the main charge. Composition B is composed of 60% military-grade RDX and 39% military-grade TNT. Military-grade RDX generally contains HMX as the major impurity, with concentrations ranging from 8 to 12% (U.S. Army 1984). Military-grade TNT is about 99% 2,4,6-TNT with the remainder made up of other isomers of TNT, the various isomers of dinitrotoluene (2,4-DNT being the most abundant), 1,3-dinitrobenzene, and 1,3,5-trinitrobenzene (TNB) (Leggett et al. 1977, George et al. 1999). Thus, each gre-

* Personal communication, Del Larson, Range Control, Fort Lewis, Washington, 2000.

Table 1. High-explosive load carried by munitions items commonly fired at Fort Lewis.¹

Round	DODIC ²	Main charge (g)		Supplemental charge		Pellet booster		Pellet auxiliary booster		Main charge total (g)
		RDX	TNT	HE ³	Wt (g)	HE	Wt (g)	HE	Wt (g)	
M67	G881	110.6	71.9	— ⁵	—	Tetryl	22.1	Tetryl	63.0	184.3
81-mm	C256 ⁴	571.5	371.5	— ⁵	—	—	—	—	—	943
105-mm	C445	—	2086	TNT	136	—	—	—	—	2086
105-mm	C445 ⁴	1252	814	TNT	132	—	—	—	—	2086
120-mm	C623 ⁴	1790	1170	—	—	—	—	—	—	2990
120-mm	C788	—	2100	—	—	—	—	—	—	2100
107-mm	C697	1252	814	TNT	132	—	—	—	—	2086
155-mm	D544 ⁴	4191	2725	TNT	136	—	—	—	—	6916
155-mm	D544	—	6622	TNT	136	—	—	—	—	6622

¹ Source of data is the Munitions Items Disposition Action System (MIDAS) and personal communication, Mark Serben, Office of the Product Manager for Mortar Systems, TACOM, Picatinny Arsenal, New Jersey, 19 March 2000.

² Department of Defense Identification Code.

³ High explosive.

⁴ Main charge is Composition B, which is typically composed of 60 percent RDX and 39 percent TNT.

⁵ Not present.

nade contains about 100 g of RDX, 11 g of HMX, and 72 g of TNT in the main charge. The detonator in the M67 also contains 1.3 g of RDX and thus each grenade contains a total of about 101 g of RDX, 11 g of HMX, 72 g of 2,4,6-TNT, with less than a gram of 2,4-DNT, TNB, and other impurities. The mass of the various high-explosive chemicals present in the M67 grenade and other ordnance commonly fired at Fort Lewis is provided in Table 1. The M26 grenade contains about 84 g of RDX, 9 g of HMX, 60 g of TNT, and 0.6 g of 2,4-DNT and other impurities.

The soil in the grenade impact area is a coarse gravelly sand with stones as large as 15 cm (Table 2). Grasses sparsely cover areas not recently affected by range use. The four impact areas within the grenade range are consecutively numbered, and from the numbers of craters

in each, have been used to a similar extent. We chose Range 3 for extensive soil sampling. Range 3 is approximately 11 m wide at the launch end (Fig. 1). The side-walls that enclose the impact area widen to approximately 25 m where they ended some 25 m from the launch bunker. The presence of a number of craters indicated that grenades had landed well beyond this 25-m distance. The range was heavily cratered indicating extensive use. Over the last four years EOD cleanup practices (detonation of duds and low-order detonations) involved the use of C-4 explosive (RDX). In years prior to the use of C-4, TNT was used for this activity.

Within Range 3, three lanes perpendicular to the launching bunker were laid out for soil sampling. These lanes were located at 15, 20, and 25 m from the launching area (Fig. 2). At a distance of 15 m from the launch

Table 2. Physical characteristics of Fort Lewis soils.¹

Sample location	TOC ² (%)	CEC ³ (meq 100 g ⁻¹)	Total Fe ⁴ (mg kg ⁻¹)	Total inorganic N ⁵ (mg kg ⁻¹)	pH	Particle size distribution (%)		
						Sand	Silt	Clay
Artillery range								
Firing point	11.3	47.4	1,530	1,530	5.6	63.2	17.5	19.3
Impact area	7.38	38.0	1,960	3,484	5.7	64.7	19.2	16.1
Hand grenade range								
Surface	0.26	6.8	3,030	175	6.8	82.3	7.8	9.9
Subsurface	0.12	6.8	2,010	151	7.0	84.6	4.5	10.9

¹ Values represent a single composite of samples from each location.

² Total organic carbon.

³ Cation exchange capacity.

⁴ Total iron.

⁵ Total inorganic nitrogen.



Figure 1. Hand grenade range at Fort Lewis, looking toward the throwing area.



Figure 2. Hand grenade range at Fort Lewis. Tape extends perpendicular from launch area. Note sample jars in rows perpendicular to tape.

site, soil samples were collected at 6.2, 7.4, 8.8, 10.1, and 11.3 m from a reference wall that separated Range 3 from Range 2. At a distance of 20 m, samples were collected at 6.2, 7.8, 9.1, and 10.2 m from the reference wall in a similar manner. Also at 20 m, a wheel-shaped 1.2-m-diameter sheet of plastic was placed on the ground and six equally spaced surface soil samples were

collected around the circle and one surface soil sample was collected in the middle of the circle, 11.5 m from the wall (Jenkins et al. 1996). At a distance of 25 m, samples were collected at 6.3, 7.7, 8.6, 10.0, 11.2, 12.0, and 13.4 m from the reference wall. At each sampling location a surface sample (0–0.5 cm) and a discrete depth (10 cm) sample was collected except for the sam-

ples collected in the wheel pattern, where only surface samples were collected. All soil samples were collected using stainless-steel trowels that were carefully wiped with a clean paper towel, washed with acetone, and air-dried between samples. About 50 g of soil was collected for each sample.

We noticed a deep (approximately 93 cm) crater approximately 30 m from the launch bunker, its depth possibly the result of multiple impacts or EOD activity. The bottom of the crater appeared to represent undisturbed native subsoil, its finer grain being much different from the overlying gravel. A surface sample was collected at the bottom of the crater and then at 10-, 15-, 23-, and 30-cm depths below surface. We were careful to remove the overlying soil and then collect the samples at the discrete depths indicated. It was noted that the samples taken from the bottom of this crater were moist whereas the surface samples were quite dry.

The most distant crater from the launch area, at approximately 45 m, was selected for sampling to represent the effect of minimal range use. One composite surface soil sample was collected from the rim of the crater, one surface sample at the bottom of the crater, and a discrete depth (10 cm) sample was collected from the bottom of the crater. A total of 48 samples was collected within the Fort Lewis hand grenade range impact area.

While sampling the grenade range, we observed what appeared to be evidence of several low-order detonations, where large portions of the grenade case were still intact. These grenade casings were collected and returned to our laboratory for analysis.

Artillery range firing point

The day before we were scheduled to sample the artillery range impact area at Fort Lewis, the active artillery firing area at Fort Lewis (R74) was being used by National Guard units for 105-mm howitzer practice. The various units had eight howitzers set up and had been firing for six weeks. Approximately 600 of the 105-mm rounds had been fired through each of the how-

itzers prior to our collecting the soil samples. The rounds being fired had the following information on their storage container: (Comp B, C445, M2A2, M 103, Cart 105, HEM1, dual grain with supply charge without fuse for HOW). The propellant being used for these rounds is composed of 85% nitrocellulose, 9% dinitrotoluene, 5% dibutylphthalate, and 1% diphenylamine. The area in front of two of the howitzers (referred to as Howitzer #1 and Howitzer #2) was chosen for firing point sampling. Both howitzers were aimed approximately 200° true into the 91st Division Prairie Artillery Impact Area. The firing area was grass-covered with various shrubs and low trees. Dirt access roads passed in front of the guns and were sampled when within the sampling scheme. All surface soil samples collected included the top 0.5 cm of soil as well as the associated surface organic matter and shallow roots when this material was present. One surface soil sample was collected approximately 400 m to the east from the nearest gun (Howitzer #1) to serve as an estimate of background contamination within the area from other firing events.

Howitzer #1

A measuring tape was placed on the ground extending from the front of Howitzer #1 in the direction of fire. Using a putty knife, surface soil samples (about 10 cm²) were collected along the measuring tape at the following distances from the muzzle: 0.5, 1.0, 1.5, 2.0, 2.5, 5.0, and 10.0 m (Fig. 3). Similar samples were also collected on both sides perpendicular to the muzzle of the howitzer at distances of 1.5 and 3.0 m. Surface soil

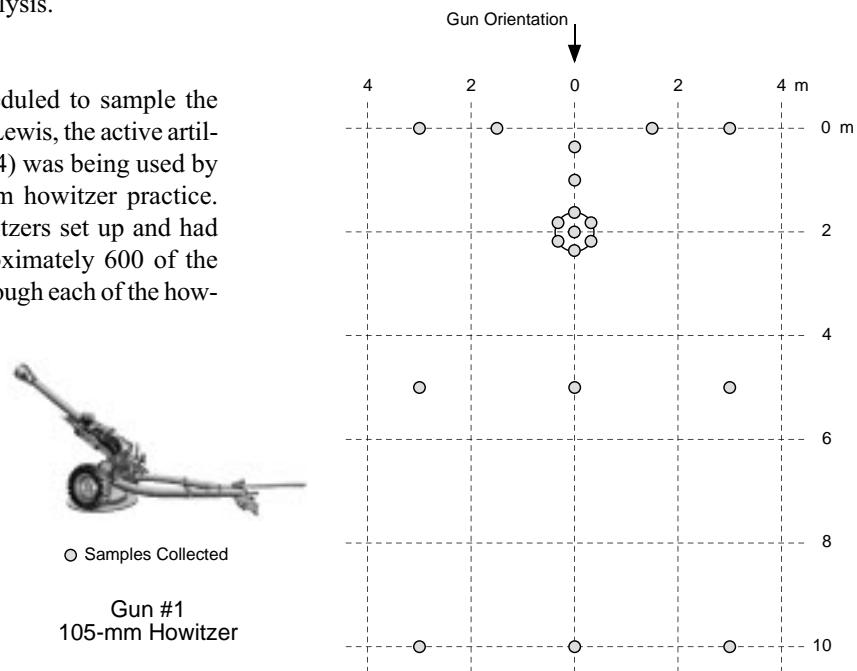


Figure 3. Surface soil samples collected at firing point in front of the muzzle of 105-mm Howitzer #1.

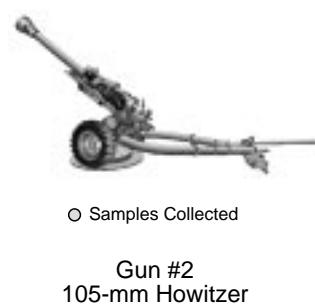
samples were also collected 3.0 m perpendicular, on both sides, to the direction of fire at distances of 5.0 m and 10.0 m. The final soil sampling took place two meters in front of the muzzle where a wheel-shaped 1.2-m-diameter sheet of plastic was placed on the ground and a set of seven samples was collected in a wheel pattern in a manner similar to that described for the hand grenade range. Also, two depth samples, 0–5 cm and 5–9 cm, were collected in the center of the circle. This sampling scheme produced a total of 22 surface and two different depth soil samples at Howitzer #1 (Fig. 3).

Howitzer #2

A measuring tape was placed on the ground in front of Howitzer #2 in the direction of fire. Using a putty knife, surface soil samples were collected along the measuring tape at the following distances from the muzzle: 0.5, 1.0, 1.5, 2.0, 2.5, 5.0, 10.0, 15.0, and 20.0 m. Surface soil samples were also collected on both sides perpendicular to the muzzle of the gun at distances of 1.5, 3.0, and 6.0 m. Surface soil samples were also collected on both sides 3.0 m perpendicular to the direction of fire at distances of 5.0, 10.0, 15.0, and 20.0 m from the muzzle. This sampling scheme produced a total of 23 soil samples at Howitzer #2 (Fig. 4).

Artillery range impact area

The artillery impact area (91st Division Prairie) at Fort Lewis consists of approximately 3800 hectares. The portion of the impact range chosen for sampling was approximately 1 km in diameter and was centered at the approximate impact point for the 105-mm howitzers described earlier. Soil sampling was conducted on 8 July 2000. We were escorted by two EOD technicians from the 707th Ordnance Disposal Company at Fort Lewis who assisted us, not only in matters of safety, but in providing their opinion on the type of round that had created specific craters, as well as estimating the age of each. They made these judgements based on the



metallic debris found in the crater, the presence or absence of ash, and the degree of weathering that had occurred around the rim of the crater. Soil from the impact area was characterized and results are presented in Table 2. Vegetation in the area sampled consisted mainly of grasses and various low shrubs and a few widely scattered small evergreen trees. Samples were collected throughout this area around various points of interest. EOD personal were invaluable at determining the specific type of munition that caused particular craters, as well as estimating the age of these craters. The most recent craters were produced the day before sampling from the impact of 105-mm howitzer rounds. Also considered recent (within the last month) were several mortar craters from various size rounds. Also, several older craters were sampled that appeared to vary in age from months to years, and which were produced by various size artillery and mortar impacts.

The sampling of craters generally consisted of collecting surface soil randomly spaced around the rim of the crater, around the inside sloping surface of the crater, and at the bottom of the crater. With the assistance of the EOD team, several soil samples were collected around and below a 155-mm artillery low-order detonation round, and three surface soil samples were collected around a low-order 120-mm mortar round. Several samples and the associated surface organic matter were collected in areas that were overgrown with vegetation and had no apparent disturbance within several meters. Numerous surface soil samples and some depth

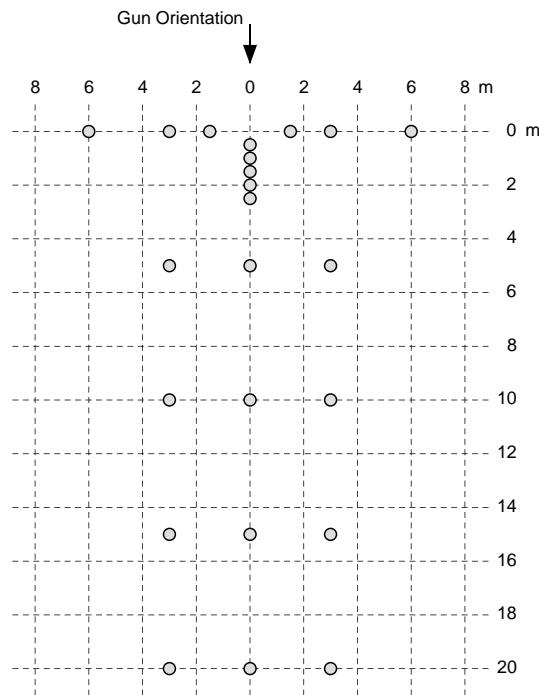


Figure 4. Surface soil samples collected at firing point in front of the muzzle of 105-mm Howitzer #2.

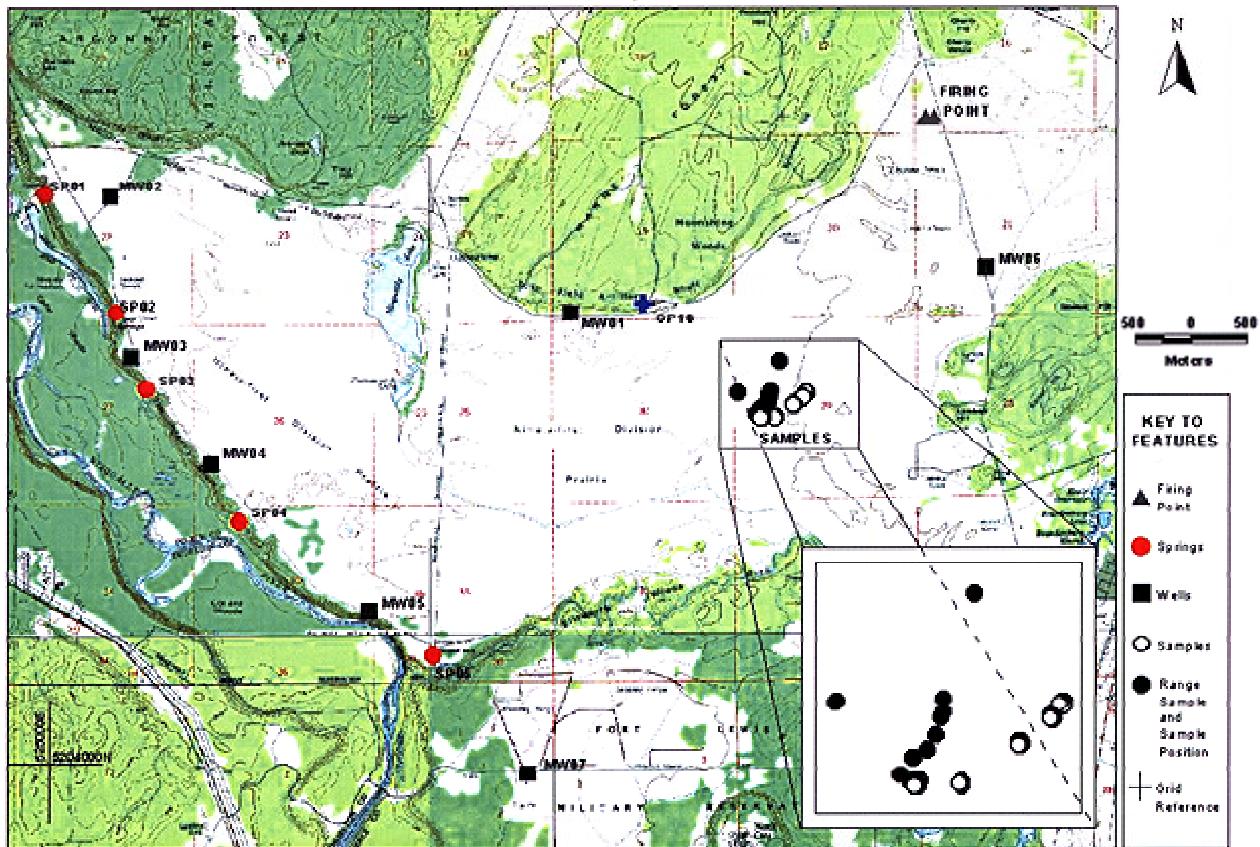


Figure 5. Locations where soil and water samples were collected at the artillery range at Fort Lewis, Washington.

samples were collected as deemed appropriate. Five areas were sampled using the wheel sampling scheme described earlier. Some of the areas that were sampled using this approach were centered over a crater and some were between craters. A total of 70 samples was collected within the artillery impact area.

Groundwater sampling from monitoring wells and seeps

Water samples were collected at Fort Lewis from five groundwater monitoring wells (MW1–MW4 and MW7) and five seeps (A1ASPO1–A1ASPO5, Fig. 5) on 27 and 28 August 2000. The wells were sampled by micropurge (low-flow) techniques using a low-flow pump. Groundwater was discharged via Teflon-lined tubing. Tubing was dedicated to each well to prevent contaminant carryover from one well to the next. The sampling pump was decontaminated between wells by purging with a mild detergent and clean water. Samples from each location were collected in a single 4-L brown glass bottle, thoroughly mixed, and subdivided into separate bottles already containing appropriate preservatives for the specific analyses (see analytical chemistry below). Samples for explosives were preserved with 1.2 g of NaHSO₄ to 1 L water (Jenkins et al. 1995).

The collection bottle was rinsed three times with deionized water between samplings. The subsamples were distributed as follows: two 1-L samples for explosives, a 500-mL sample for nitrate/nitrite, total organic carbon, total iron, calcium, magnesium, and manganese, and a 100-mL sample for sulfate and chloride. Seepage areas were sampled by placing the sample container into the stream of discharge. Field parameters were measured with a hand-held monitoring unit (Horiba U10, Horiba Instruments, Irvine, California). Field parameters included pH, conductivity, dissolved oxygen (DO), and temperature. Samples were obtained when consecutive DO readings were within 10 percent of each other. The samples were split by ERDC-EL personnel, one aliquot of each sample going to the contract laboratory, and the second going to ERDC-CRREL. Three of the samples were also split and sent to the analytical chemistry laboratory at ERDC-EL.

SITE DESCRIPTION AND SOIL SAMPLING, FORT RICHARDSON, ALASKA

United States Army Garrison Alaska consists of the three posts of Fort Richardson (Anchorage), Fort Wainwright (Fairbanks), and Fort Greely (Delta Junction).

Fort Richardson borders Anchorage, Alaska, to the west and north. The Garrison headquarters is located at Fort Richardson, as is the headquarters of the United States Army Alaska (USARAK). The garrison supports rapid deployment of the 172nd Separate Infantry Brigade and elements of the Arctic Support Brigade within the Pacific theater, and worldwide as directed in support of Pacific Command's (USARPAC) objectives, U.S. national interests, and contingency operations. Fort Richardson encompasses 62,000 acres, with 47,000 acres available for training. Military assets within that area include a heliport, a drop zone suitable for airborne and airland operations, firing ranges, and other infantry training areas.

Sampling at Fort Richardson was limited to the hand grenade range. The grenade range is located in the small arms complex near the Glenn Highway. The grenade range is not divided into individual bays, but is a single open area with six launching bunkers and a large rubber tire 35 m downrange of each to serve as a target. The surface soil is mainly gravel and any craters formed during training are filled with fresh gravel at the end of each exercise. Soil samples were collected from the Fort Richardson grenade range on 20 October 2000. The top surface of the soil was frozen, but the soil just beneath the surface was thawed at the time of collection.

The grenade range at Fort Richardson has six launching bunkers and six associated target areas marked with a large rubber tire. The area between Targets 1 and 2 was selected for sampling. Since surface craters are filled in with gravel after each exercise, there were no visual clues to the intensity of use of each area. The protocol for use of the range, however, was said to utilize the six areas equally.

Training at the Fort Richardson grenade range involved mainly the use of M67 hand grenades, although occasionally claymore mines were used as well. Over the three-year period a total of 5000 M67 grenades and 90 claymore mines have been detonated on site. Since there are six launching areas at this range, this amounts to about 300 per year per launch area. This is only about 20% of the detonations in a comparable area at the Fort Lewis range.

Soil samples were collected as follows. A set of four samples was collected at 27 m from the launching point (Fig. 6). These samples were collected at the surface, at a 15-cm depth, a 30-cm depth, and a 45-cm depth. A second set of four samples at the same depths was also taken 27 m from the launch area, 1 m to the left of the first set. Additional sets of four samples were collected

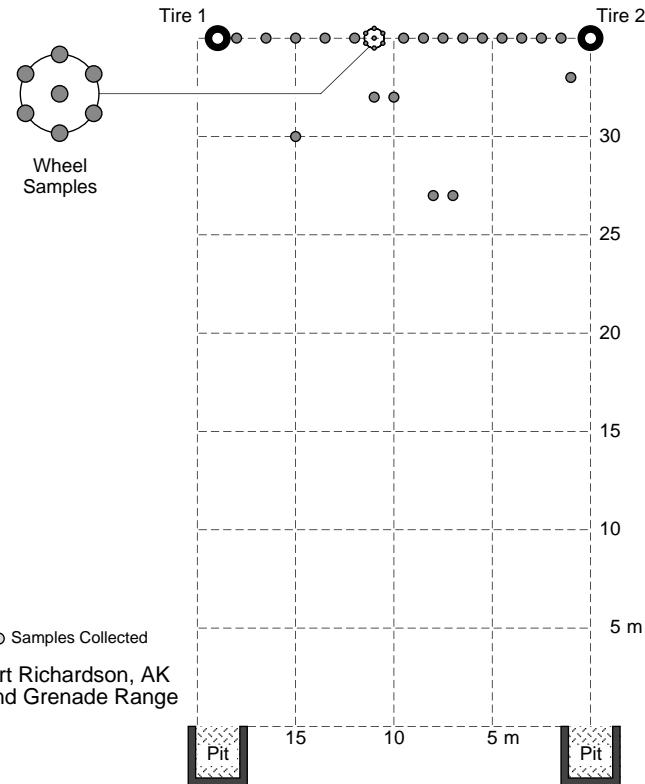


Figure 6. Position of soil samples collected at the hand grenade range at Fort Richardson, Alaska.

in an identical manner at distances of 30, 32, and 33 m from the launch area. A set of 15 surface soil samples was collected at 35 m, on the line between the two target tires, each sampling point separated by 1 m from the last. Centered at the tenth position, a seven-sample sampling wheel, like that described for samples at Fort Lewis, was collected for surface soil. At the center position, three depth samples were also collected at 15, 30, and 45 cm. The total of 48 soil samples was collected at the Fort Richardson grenade range. Because of the gravelly consistency of the surface soil in the Fort Richardson hand grenade range, all soil samples were collected using shovels.

EXPERIMENTAL METHODS AND MATERIALS

Soil sample collection and shipment

All soil samples at Fort Lewis were collected using stainless-steel trowels or putty knives that were carefully wiped with clean towels, washed with acetone, and air-dried between samples. Shovels were used for sampling at Fort Richardson and they were cleaned in a similar manner. As samples were collected they were placed in precleaned, amber, straight wall jars. Each jar was placed in a Ziploc bag and shipped to the labo-

ratory in ice-filled coolers (FedEx overnight). Upon arrival at CRREL the samples were frozen at -30°C until extraction and analysis within two weeks.

Soil extraction

For extraction, the jars containing the soil samples were moved to the laboratory and allowed to warm to room temperature. Samples were homogenized by removing small stones, breaking up the material in the sample jar using a spatula, and stirring the contents thoroughly. The sample sometimes consisted of just soil but usually was a combination of both soil and organic matter. A 2.00-g portion of undried material was then removed from the jar in several increments and placed in a 22-mL scintillation vial. A 5.00- or 10.0-mL aliquot of AcN was added to each sample, depending on the amount of organic matter present. The vials were then placed on a vortex mixer for 30 seconds to suspend the soil particles, and the vials were placed in an ultrasonic bath for 18 hours. The temperature of the bath was maintained at less than 25°C with cooling water. The vials were then removed from the bath and allowed to stand undisturbed for 30 minutes. A 2.5-mL aliquot of each extract was removed using a glass syringe and filtered through a 25-mm Millex-FH (0.45-µm) disposable filter, discarding the first milliliter and collecting the remainder in a clean autosampler vial. The extracts were kept cold prior to and during analysis.

Soil extract analysis

The vials containing the AcN (acetonitrile) soil extracts were placed into GC autosampler trays that were continuously refrigerated by circulating 0°C glycol/water through the trays. The extracts were analyzed by gas chromatography using a micro-electron capture detector (GC-µECD). Results were obtained on a HP-6890 GC equipped with a micro cell Ni⁶³ detector at 280°C according to the general procedure outlined in EPA SW-846 Method 8095 (draft) (EPA 2000b). Direct injection of 1 µL of soil extract was made into a purged packed inlet port, at 250°C, that was equipped with a deactivated Restek Uniliner. Primary analysis was conducted on a 6-m- × 0.32-mm-ID fused-silica column, with a 1.5-µm film thickness of 5%-(phenyl)-methylsiloxane (RTX-5 from Restek). The GC oven was temperature programmed as follows: 100°C for two minutes, 10°C/minute ramp to 260°C, two-minute hold. The carrier gas was helium at 10 mL/minute (linear velocity approximately 90 cm/sec). The ECD makeup gas was nitrogen flowing at 40 mL/minute. If a peak was observed in the retention window for a specific signature compound, the extract was reanalyzed on a confirmation column, 6-m × 0.53-mm ID having a 0.1-µm film thickness of 50% cyanopropylmethyl-50%

phenylmethyl-polysiloxane (RTX-225 from Restek). Further details of the procedure may be found in SW-846 Method 8095 (draft) (USEPA 2000b). If analyte concentrations were within the linear range of the ECD, concentrations reported were taken from the determination on the primary column, unless there appeared to be co-elution with another compound. In such cases, reported concentrations were taken from the determination of the confirmation column. Detection limits for the GC-ECD analysis were about 1 µg/kg for di- and trinitroaromatics, and 3 µg/kg for RDX (Table 3).

Table 3. Method detection limits (µg kg⁻¹) of nitroaromatics, nitramines, and nitrate esters in soil determined by GC-ECD (Walsh and Ranney 1999).

Analyte	MDL (µg kg ⁻¹)
1,3-Dinitrobenzene	0.8
2,6-Dinitrotoluene	0.8
2,4-Dinitrotoluene	0.8
1,3,5-Trinitrobenzene	3
2,4,6-Trinitrotoluene	1
RDX	3
4-Amino-2,6-dinitrotoluene	1.5
2-Amino-2,4-dinitrotoluene	2.5
Tetryl	20
HMX	25
3,5-Dinitroaniline	2
Nitroglycerin	20
PETN	25
<i>o</i> -Nitrotoluene	15
<i>m</i> -Nitrotoluene	12
<i>p</i> -Nitrotoluene	10

Extracts were also analyzed by RP-HPLC according to SW-846 Method 8330 (EPA 1994). When concentrations were above 500 µg/kg, the reported concentrations were taken from the HPLC analysis, which had a higher range of linearity. The response of the GC-ECD was inadequate for the reduction products of 2,4-DNT (4A2NT and 2A4NT). Data reported for these analytes were obtained by RP-HPLC. RP-HPLC analysis was conducted on a modular system composed of a Spectra-Physics Model SP8800 ternary HPLC pump, a Spectra-Physics Spectra 100 variable wavelength UV detector set at 254 nm (cell path 1 cm), a Dynatech Model LC241 autosampler equipped with a Rheodyne Model 7125 sample loop injector, and a Hewlett-Packard 3396A digital integrator set to measure peak heights. Extracts were diluted with reagent-grade water (one part extract and four parts water). Separations were conducted on a 15-cm × 3.9-mm NovaPak C-8 column (Waters) eluted with 85/15 water/isopropanol (v/v) at 1.4 mL/minute. Samples were introduced by overfilling a 100-µL sampling loop. Concentrations were estimated against multianalyte stan-

dards using peak heights. Detection limits for 4A2NT, 2A4NT, and 3,5-DNA were about 250 µg/kg.

Analysis of fragments from low-order hand grenade detonation

A hand grenade casing that had undergone a low-order detonation was discovered at the Fort Lewis hand grenade range and was sent back to CRREL for analysis. Visually it appeared that residual Composition B, the main charge for M67 grenades, was still present on the surface of this metal casing. Small portions of the hand grenade casing were placed in 5.0 mL of acetone and allowed to dissolve for five minutes, at which time an aliquot of the acetone extract was removed for analysis. After an additional 15 minutes of soaking, a second aliquot was removed for analysis. Both acetone extracts were diluted 1:100 with acetone and the diluted extract was further diluted 1 to 3 parts water. The resulting solutions were analyzed using the separations described in SW-846 Method 8330 (EPA 1994).

Analysis of water samples from monitoring wells and seeps at Fort Lewis

At CRREL, the water samples were extracted using solid-phase extraction as described in SW-846 Method 3535A (draft) (EPA 2000c). Specifically, 500 mL of each sample was passed through a 500-mg Sep-Pak Porapak RDX cartridge (Waters) and the retained analytes were eluted using 5.0 mL of acetonitrile. The extracts were analyzed by GC-ECD as described above for soil extract analysis.

At ERDC-EL, the water samples were also extracted using solid-phase extraction as described above. Analyses were conducted by RP-HPLC-UV according to SW-846 Method 8330 (EPA 1994) on a Waters system composed of a Waters 610 Fluid Unit pump, a Waters 717 plus autosampler with a 200-µl loop injector, a Waters 486 Tunable UV Absorbance detector monitored at 245 nm, and Millennium 2.1 Chromatography Software (Waters Chromatography Division, Milford, Massachusetts). Separations were obtained on Supelco LC-18 reverse-phase HPLC column 25 cm × 4.6 mm (5 µm) with second column confirmation on a Supelco LC-CN reverse phase column (25 cm × 4.6 mm, 5 µm). Additional transformation products of TNT and TNB assayed by the ERDC-EL laboratory included 3,5-dinitroaniline (DNA), 2,4-diamino-6-nitrotoluene (2,4DANT), and 2,6-diamino-4-nitrotoluene (2,6DANT) and 2,2,6,6-tetranitro-4,4-azoxyltoluene (44AZOXY). Additional transformation products of RDX assayed by the ERDC-EL laboratory included hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro, 1,3,5-trinitroso-1,3,5-triazine (TNX), and hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX).

At the contract laboratory, the samples were also analyzed by RP-HPLC according to SW-846 Method 8330 (EPA 1994).

Laboratory analyses for geochemical parameters included total iron, calcium, magnesium, and manganese (Method 6010, U.S. EPA 1988), total organic carbon (Method 505C, American Public Health Association 1985), nitrate/nitrite nitrogen (Method 353.2, U.S. EPA 1982), sulfate (Method 375.2, U.S. EPA 1982), and chloride (Method 325.2, U.S. EPA 1979). Samples for total iron, calcium, magnesium, and manganese, total organic carbon, and nitrate/nitrite nitrogen were preserved with 0.4 g NaHSO₄ to 250 mL of water. Samples for sulfate and chloride were not preserved. Iron speciation was achieved by ion chromatographic separation (Dionex Corp., Sunnyvale, California) of samples preserved with 1 percent HCl followed by analysis according to Method 6020, (U.S. EPA 1988) on a Perkin Elmer (Norwalk, Connecticut) inductively coupled plasma mass spectrometer.

Historical firing records

Historical firing records contained in an electronic database at Fort Lewis were reviewed to understand the major components potentially contributing to an explosives contamination source term on the heavy artillery impact range. These records were available from 1997 through the time of sampling, July 2000. Only munitions items identified by the Fort Lewis Range Operations Office as “high use” were included. These were 81-, 120-, and 107-mm mortars and 105-and 155-mm howitzers. The database provided the number of rounds by Department of Defense Identification Code (DODIC) number, date, and location where firing was scheduled to occur. Composition of these rounds was determined by consulting the Munitions Items Disposition Action System (MIDAS) and Mark Serben, Office of the Product Manager for Mortar Systems, TACOM, Picatinny Arsenal, New Jersey. The dud and low-order detonation rates for these munitions were extracted from the data generated by the U.S. Army Defense Ammunition Center, McAlester, Oklahoma (Dauphin and Doyle 2000).

RESULTS AND DISCUSSION

Hand grenade ranges, Fort Lewis and Fort Richardson

The results from the analysis of the soil samples collected from the Fort Lewis hand grenade range are presented in Table 4. Of the 19 target analytes of the method, RDX, TNT, HMX, 2,4-DNT, 2-ADNT, 4-ADNT, 1,3,5-TNB, 2,6-DNT, and 3,5-DNA were found at concentrations exceeding 10 µg/kg (10 parts per bil-

Table 4. Explosives in soils from Fort Lewis hand grenade range ($\mu\text{g kg}^{-1}$).¹

Sample	Location ²		RDX	HMX	TNT	2,4DNT	2,6DNT	4ADNT	2ADNT	1,3,5TNB	3,5-DNA
	From reference (m)	Depth (cm)									
15 m from launch point											
137	6.2		689	365	329	38.2	2.2	147	140.8	89.4	28.2
138	6.2	10	86	t ³	128	22.5	<0.8 ⁴	150	274	<3	56.8
139	7.4		11,900	1,120	4,230	16.9	2.2	180	163	<3	44.6
140	7.4	10	76	<25	33.9	7.5	<0.8	63.5	58.7	<3	18.0
141	8.8		990	172	79.9	18.7	1.7	95.2	91.3	55.2	20.2
142	8.8	10	235	<25	61.1	<d	<0.8	23.8	13.7	22.4	2.85
143	10.1		1,730	1,590	374	92.0	2.3	322	273	56.8	11.5
144	10.1	10	385	60.9	33.8	11.5	1.0	38.7	43.9	33.9	15.8
145	11.3		1,640	813	51.1	13.7	2.4	146	128	50.4	23.3
146	11.3	10	369	77.8	263	5.5	1.7	75.6	83.4	16.0	24.3
20 m from launch point											
129	6.2		316	232	17,700	18.1	1.6	74.1	51.5	<3	<2
130	6.2	10	107	<25	67.4	5.7	1.6	35.7	<2.5	<3	<2
131	7.8		1,660	332	941	17.7	5.0	95.5	68.8	<3	<2
132	7.8	10	117	60.3	74.8	11.5	1.1	71.8	89.4	33.4	37.7
133	9.1		6,230	294	75,100	78.3	3.1	130	130	<3	34.5
134	9.1	10	97	66.0	42.0	8.1	0.8	28.1	37.6	25.4	7.2
135	10.2		503	239	264	30.6	1.7	149	167	98.0	24.1
136	10.2	10	202	49.7	21.0	7.1	<0.8	37.8	46.5	11.4	24.7
122	11.5 C ⁵		1,940	1,210	293	19.2	3.1	94.1	23.3	<3	<2
123	A		424	455	126	16.6	3.0	80.3	60.8	<3	<2
124	B		28,000	3,900	40,300	24.3	2.8	250	231	<3	<2
125	C		1,260	625	40,600	31.3	2.2	83.7	14.7	<3	<2
126	D		1,100	761	379	32.0	2.8	111	88.0	<3	<2
127	E		1,630	1,030	333	9.4	2.0	66.6	55.5	<3	<2
128	F		1,750	1,170	4,470	11.6	1.2	83.1	64.0	<3	<2
25 m from launch point											
147	6.3		1,030	642	563	17.5	3.1	153	138	124	26.5
148	6.3	10	187	45.2	72.2	6.1	0.9	75.0	97.3	36.1	32.4
149	7.7		1,050	436	1,050	69.2	2.2	125	132	126	32.3
150	7.7	10	261	91.3	45.2	7.8	110	47.6	57.5	44.5	20.4
151	8.6		1,380	2,330	95.3	17.5	2.6	80.2	74.8	149	29.5
152	8.6	10	186	82.7	22.1	4.6	1.0	25.7	31.4	36.0	14.0
153	10		2,530	1,450	255	37.8	2.7	144	164	134	37.8
154	10	10	179	<25	11.9	5.2	1.8	29.6	31.6	15.4	15.0
155	11.2		27,700	5,810	10,800	26.6	4.7	173	196	<3	16.7
156	11.2	10	7,390	1,540	2060	28.3	2.1	258	245	<3	19.6
157	12.0		51,200	10,100	15,800	33.0	33.2	388	298	<3	67.5
158	12.0	10	864	57.1	29.9	3.9	1.5	26.0	35.5	<3	16.1
159	13.4		24,700	5,220	522	39.6	5.1	279	281	214	34.3
160	13.4	10	243	42.5	80.2	5.8	1.4	32.8	55.1	38.5	18.1
Deep 93-cm-diameter crater 30 m from launch point											
161	Bottom surface		1,690	329	153	10.1	1.6	96.3	98.0	69.6	9.2
162		10	684	230	120	10.1	<0.8	109	113	39.6	6.5
163		15	626	346	214	8.8	1.3	126	116	31.1	<2
164		23	775	197	197	10.1	1.6	111	115	38.5	<2
165		30	234	91.0	99.4	8.7	1.4	51.8	67.4	31.9	4.4
Approximately 45 m from launch point											
166	Crater c/B ⁶	18.1	t	5.65	2.9	1.2	21.3	25.5	t	3.7	
167	Crater R/cp ⁷	70.5	t	5.63	<0.8	1.4	24.4	27.7	<3	5.0	
168	Crater c ⁸	10	25.0	t	5.58	1.5	<0.8	28.9	38.0	<3	3.7

¹ Values given are for surface soils except where noted. The following undetected analytes were excluded from the table: 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 1,3-dinitrobenzene, nitroglycerin, 2,5-dinitrotoluene, 3,4-dinitrotoluene, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

² Locations give distance from reference wall separating impact areas for each range and depth in cm if sample was not taken at the surface.

³ Trace detected below mean detection limit.

⁴ Less than detection limits.

⁵ Wheel pattern of sampling: C = center of wheel; A–F clockwise around wheel circumference.

⁶ Center, bottom of crater.

⁷ Rim, composite.

⁸ Center.

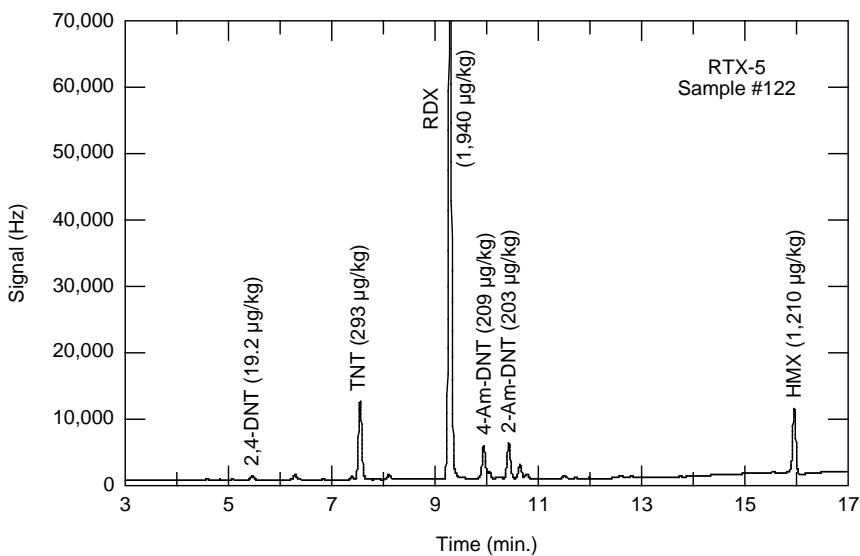


Figure 7. GC-ECD chromatogram from a soil sample collected at the Fort Lewis hand grenade range.

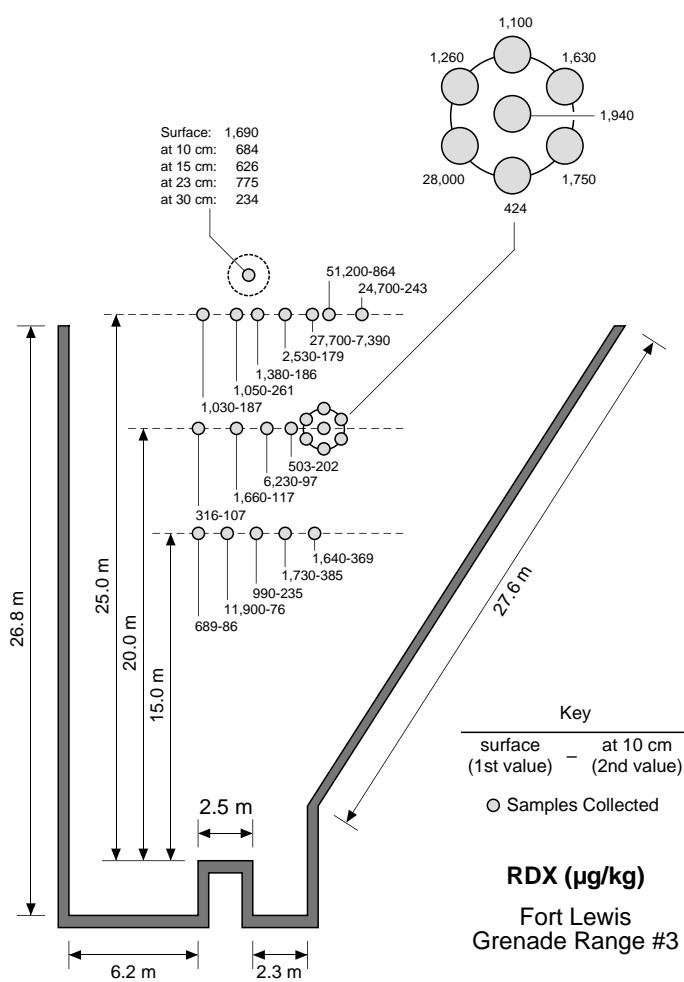


Figure 8. Concentrations of RDX for soil samples collected at the hand grenade range at Fort Lewis, Washington.

lion) in at least one sample. RDX, TNT, and 4-ADNT were detected in every sample analyzed from the Fort Lewis grenade range. RDX, TNT, and HMX were consistently found at the highest concentrations with maximum values of 51,200 µg/kg, 75,200 µg/kg, and 10,100 µg/kg, respectively. A GC-ECD chromatogram for an extract of one of the surface soils from the hand grenade range is shown in Figure 7. Diagrams showing the concentrations of RDX, TNT, and HMX for these samples are shown in Figures 8, 9, and 10.

For the surface/10-cm-depth sample pairs, the concentrations were consistently higher in surface samples than in samples collected at the 10-cm depth. Because in neither case were the values normally distributed, for the following discussion we will use ranges and median values for each analyte, rather than means and standard deviations. For example, the range of concentrations of RDX for surface soil samples was 316 to 51,200 µg/kg with a median concentration of 1,560 µg/kg, while the range of values for the 10-cm samples was 76 to 7,390 µg/kg with a median value of 195 µg/kg.

Likewise, the range of surface concentrations of TNT was 51 to 75,100 µg/kg with a median value of 543 µg/kg. At 10 cm, TNT concentrations ranged from 12 to 2,060 µg/kg with a median value of 56 µg/kg. Surface concentrations of HMX ranged from 172 to 10,100 µg/kg with a median concentration of 728 µg/kg while at 10 cm, HMX concentrations ranged from <1 to 1,540 µg/kg with a median concentration of

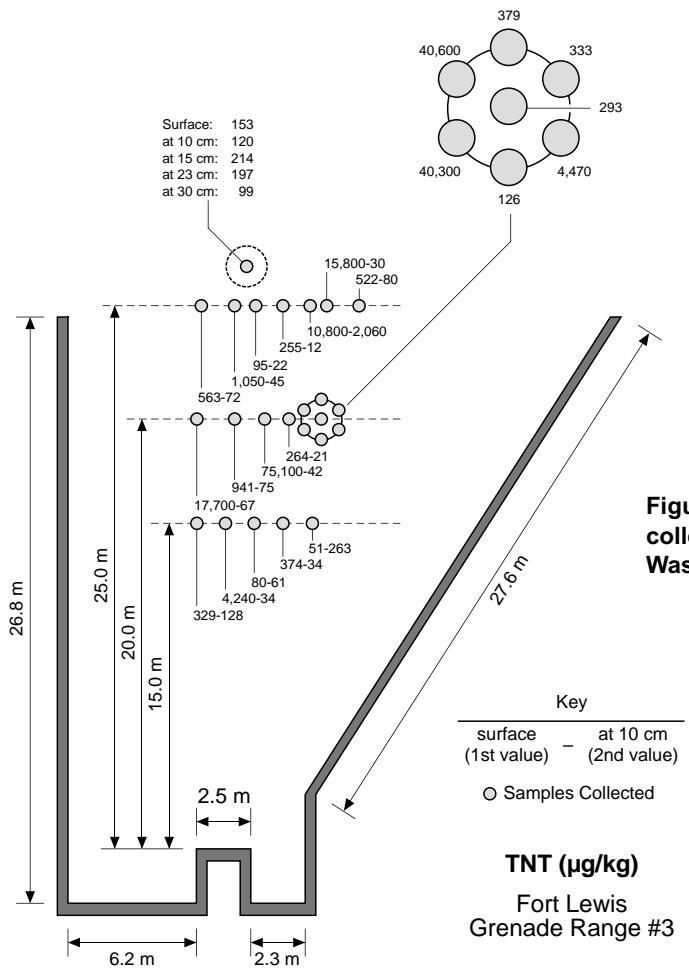


Figure 9. Concentrations of TNT for soil samples collected at the hand grenade range at Fort Lewis, Washington.

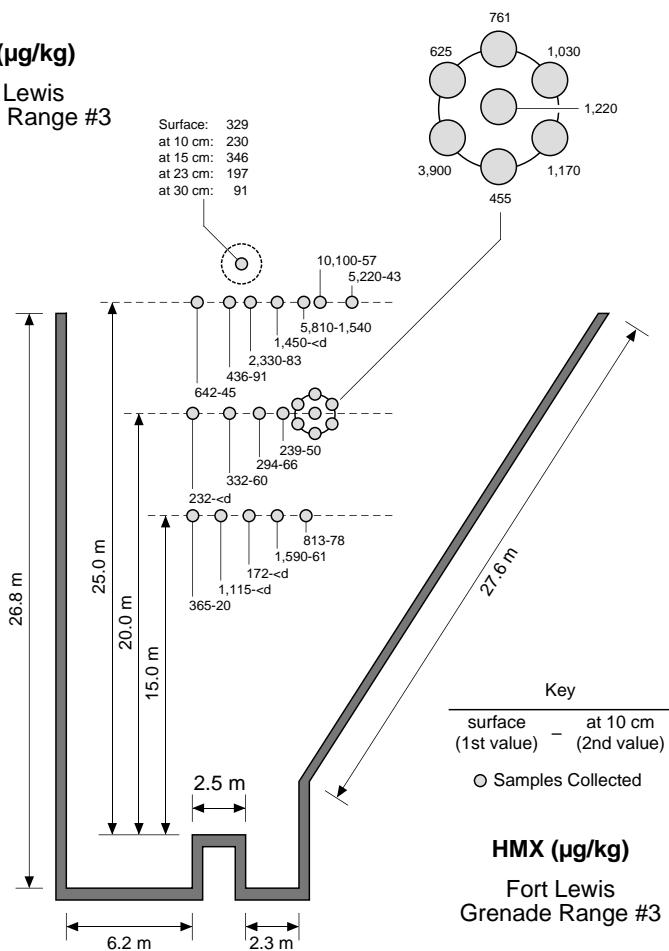


Figure 10. Concentrations of HMX for soil samples collected at the hand grenade range at Fort Lewis, Washington.

Table 5. Explosives in soils from Fort Richardson hand grenade range ($\mu\text{g kg}^{-1}$).¹

Sample number	Location ²				RDX	TNT	4ADNT	HMX
	From reference (m)	From launch (m)	Depth (cm)					
1	27	7			78.5	56.1	26.3	t ³
2	27	7	15		19.8	<1 ⁴	t	t
3	27	7	30		10.8	t	t	t
4	27	7	45		4.3	t	<1.5	t
5	27	8			14.9	2.9	2.1	t
6	27	8	15		24.1	<1	<1.5	t
7	27	8	30		5.2	<1	<1.5	<25
8	27	8	45		4.3	<1	<1.5	<25
9	33	1			518	52.0	4.1	36.9
10	33	1	15		193	3.4	1.9	t
11	33	1	30		3.1	<1	<1.5	<25
12	33	1	45		42.1	2.7	<1.5	<25
13	32	10			11.8	1.5	4.1	t
14	32	10	15		4.2	<1	<1.5	<25
15	32	10	30		8.0	<1	<1.5	<25
16	2	10	45		t	<1	<1.5	<25
17	Wheel center	35			106	50.2	43.6	t
18	Wheel				61.2	9.7	12.8	t
19	Wheel				18.1	5.9	9.4	t
20	Wheel				49.5	20.4	17.3	t
21	Wheel				22.1	6.7	8.2	t
22	Wheel				12.0	3.9	6.9	t
23	Wheel				46.5	27.0	12.4	t
24	Wheel center ⁵	35	15		t	<1	<1.5	<25
25	Wheel center ⁵	35	30		8.3	<1	<1.5	<25
26	Wheel center ⁵	35	4		39.3	11.2	17.9	t
27	32	12			4.6	2.5	2.1	<25
28	32	12	15		8.6	<1	<1.5	<25
29	32	12	30		4.8	<1	<1.5	<25
30	32	12	45		4.3	<d	<1.5	<25
31	30	15			15.5	8.2	11.7	t
32	30	15	15		15.0	<1	<1.5	t
33	30	15	30		t	<1	<1.5	<25
34	30	15	45		4.3	<1	<1.5	<25
35	35	1			115	42.8	5.3	66.6
36	35	2			1.7	t	<1.5	<25
37	35	3			152	19.9	8.3	t
38	35	4			156	29.9	10.6	27.4
39	35	5			102	93.9	48.8	56.4
40	35	6			31.9	28.7	20.2	30.
41	35	7			16.5	9.3	9.2	t
42	35	8			51.0	7.2	10.1	t
43	35	9			15.6	70.6	11.6	t
44	35	11			19.7	6.8	7.3	56.9
45	35	12			28.9	6.8	10.6	80.4
46	35	13			21.6	8.5	9.0	t
47	35	14			26.1	13.8	14.5	t
48	35	15			374	134	47.5	t

¹ Values are for surface soils except where noted. The following undetected analytes were excluded from the table: nitrobenzene, *o*-nitrotoluene, *m*-nitrotoluene, *p*-nitrotoluene, nitroglycerin, 1,3-dinitrobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 1,3,5-trinitrobenzene, PETN, 3,5-dinitroaniline, tetryl.

² Locations give distances from reference wall followed by distance from launch in meters. Depth in cm is also given for samples not taken from the surface.

³ Values are trace below the mean detection limit.

⁴ Less than detection limits.

⁵ Subsurface samples.

53.4 $\mu\text{g/kg}$. The ratio of TNT to either 4-ADNT or 2-ADNT was generally higher in the surface than at the 10-cm depth, probably because the soil remained wetter at depth, thereby creating a condition more favorable to biotransformation. It is probable, though, that detonations in the sandy soil in this range mix the soil profile to some extent. Thus one 10-cm-depth sample had concentrations of RDX and TNT of 7,390 and 2,060 $\mu\text{g/kg}$, respectively.

For the surface samples collected in the wheel pattern, 20 m from the launching area, RDX concentrations ranged from 424 to 28,000 $\mu\text{g/kg}$. A chromatogram of the extract from the center sample of the wheel, analyzed on the RTX-5 column, is presented in Figure 7. Likewise, TNT concentrations ranged from 126 to 40,600 $\mu\text{g/kg}$ and HMX from 455 to 3,900 $\mu\text{g/kg}$. Thus, as found elsewhere (Jenkins et al. 1997, 1998), explosives concentrations in surface soils are spatially very heterogeneous within this range, even over short distances, and it would be impossible to obtain representative samples for establishing a mean concentration using discrete soil samples.

Results from the analysis of a hand grenade casing remaining after a low-order detonation revealed the presence of residual Composition B. The ratio of RDX to HMX in this Composition B removed from the casing was 7.61. The ratios of RDX to HMX from analysis of individual soil samples varied tremendously, but the ratio obtained using the median values for the RDX and HMX was 2.14 for the surface soil and 3.65 for soil collected at the 10-cm depth. We interpret these reduced ratios to indicate that RDX has preferentially leached deeper in the soil profile because of a higher thermodynamic solubility, as well as a faster rate of dissolution, thereby leaving a lower RDX/HMX ratio in near-surface soils than was present in the Composition B.

Results from the analysis of soil samples from the Fort Richardson hand grenade range are presented in Table 5. Detectable concentrations of RDX, TNT, 4-ADNT, and 2-ADNT were found in most surface samples. Diagrams for RDX and TNT are presented in Figures 11 and 12.

As found for the Fort Lewis range, RDX was the explosives-related analyte found at highest concentration in the 27 surface soils that were analyzed, although the concentrations found at the Fort Richardson range were generally an order of magnitude lower than those found at Fort Lewis. The reason for this difference may be the practice at Fort Richardson of filling in the craters with clean gravel after each training session, or a lower usage of the range in terms of total grenades thrown, than at the Fort Lewis range. There were several RDX concentrations in excess of 100 µg/kg at the Fort Richardson range, but the bulk of the values were below 30 µg/kg, indicating that the distribution of these data was also non-normal. Overall, RDX concentrations in the surface soil ranged from 1.7 to 518 µg/kg with a median value of 28.9 µg/kg.

RDX was detected in all of the 21 subsoil samples collected at Fort Richardson as well, with concentrations ranging from 1.8 to 42.1 µg/kg. Median values for soil samples collected at 15-, 30-, and 45-cm depths were 15.0, 5.2, and 4.3 µg/kg, respectively. These results appear to indicate that RDX is leaching downward into the soil profile at the hand grenade range, but the concentrations leaching must be very low. These residual concentrations in subsurface soils are often barely detectable, even using the new GC-ECD method with much lower detection limits than the method that had been used traditionally, RP-HPLC Method 8330. Had method 8330 been used to analyze the soils samples at Fort Richardson, explosives analytes in most samples would have been non-detects.

The distribution of TNT concentrations in surface soil samples at Fort Richardson was found to be similar to that of RDX; several values were above 50 µg/kg, but the bulk of the values was less than 20 µg/kg (Fig. 12). Here again, concentrations were an order of magnitude or more lower than those found at Fort Lewis. In surface soil samples, TNT concentrations ranged from 0.9 to 134 µg/kg with a median value of 9.7 µg/kg. The two environmental transformation products of TNT, 4-ADNT and 2-ADNT, ranged from <1 to 48.8 µg/kg and <1 to 28.0 µg/kg, respectively, with median values of 10.1 and 7.3 µg/kg. Concentrations of TNT in 16 of the 21 subsoil samples were <1 µg/kg. Likewise, concentrations of 4-ADNT and 2-ADNT were also generally <1 µg/kg, indicating that neither TNT nor its

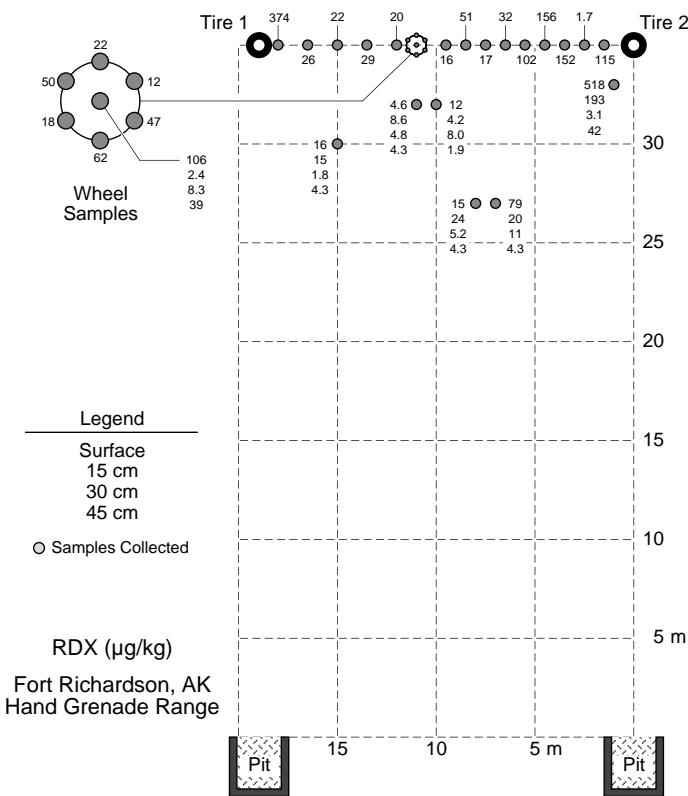


Figure 11. Concentrations of RDX for soil samples collected at the hand grenade range at Fort Richardson, Alaska.

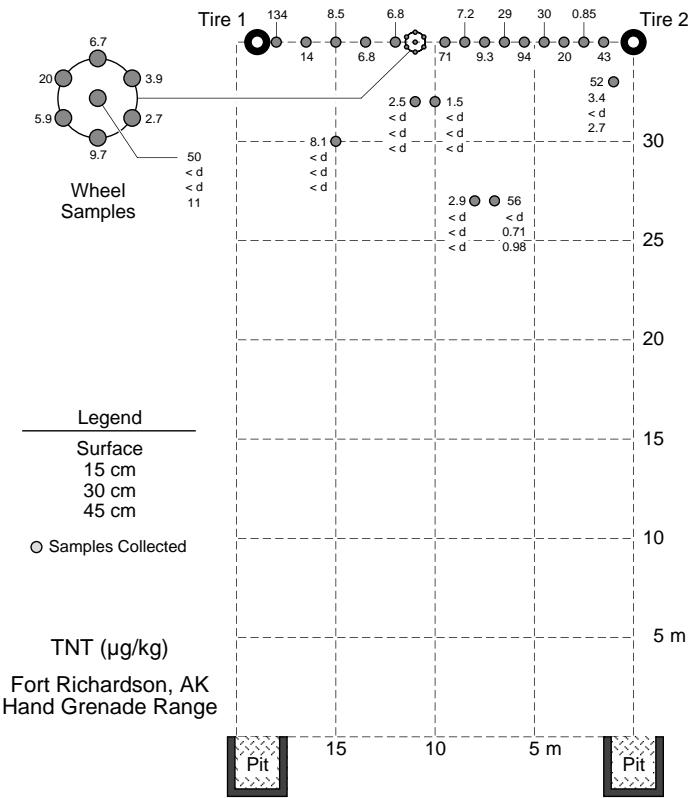


Figure 12. Concentrations of TNT for soil samples collected at the hand grenade range at Fort Richardson, Alaska.

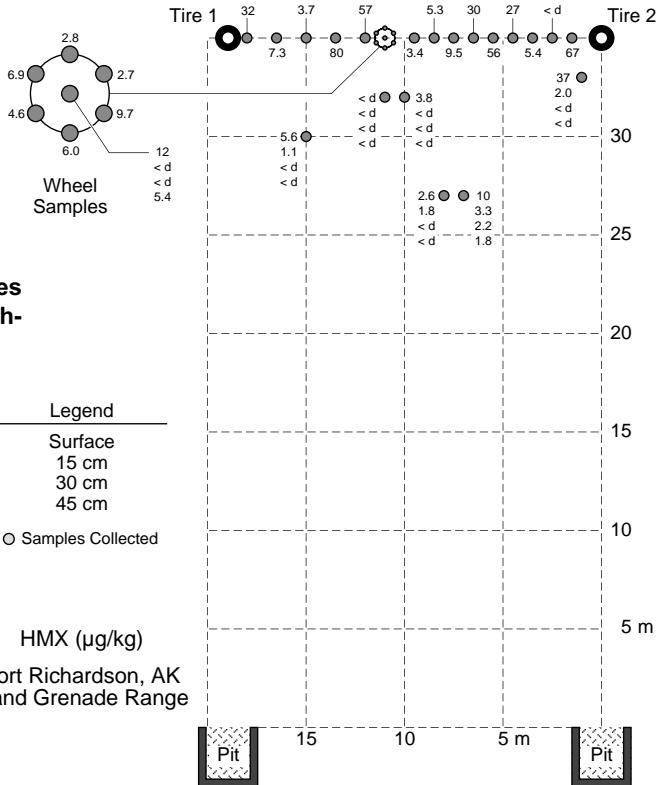


Figure 13. Concentrations of HMX for soil samples collected at the hand grenade range at Fort Richardson, Alaska.

daughter products were leaching at detectable concentrations below the surface soil. The behavior of TNT relative to RDX is not surprising since TNT and its daughter products are known to sorb to soils to a much greater extent than RDX (Brannon et al. 1999).

Concentrations of HMX in surface soils at Fort Richardson ranged from <1 to 80.4 $\mu\text{g/kg}$ with a median value of 6.9 $\mu\text{g/kg}$ (Fig. 13). A ratio of the median values for RDX/HMX in these soils is 4.2 compared with a mean ratio of 7.6 for the Composition B extracted from a low-order hand grenade. Concentrations of HMX in the subsoil were found to be <1 $\mu\text{g/kg}$ in 14 of the 21 samples analyzed. The lower solubility and rate of dissolution of HMX compared with RDX is probably responsible for a lower residual concentration ratio of RDX to HMX in surface soil than is present in Composition B, and for the higher ratio of RDX to HMX found in the subsoil samples.

Overall, subsurface concentrations of these explosives-related analytes decline rapidly below the surface soil at Fort Richardson. Because this grenade range has a much harder surface than that at Fort Lewis, we believe there is much less mixing of the soil profile and analytes found at depth were more likely to have arrived by leaching than for the subsurface samples we collected at Fort Lewis.

Artillery range firing point

Results from analysis of the 47 surface soil samples

from the artillery firing point for Howitzer #1 and Howitzer #2 are presented in Tables 6 and 7, respectively. In both cases, the major propellant-related compounds observed were the various isomers of dinitrotoluene (2,4-DNT, 2,6-DNT, 2,5-DNT, and 3,4-DNT), the two isomeric environmental transformation products of 2,4-DNT, 4-amino-2-nitrotoluene (4A2NT) and 2-amino-4-nitrotoluene (2A4NT), and 2,4,6-TNT. The presence of 2,4,6-TNT at the firing point was unexpected, and we assume it is a manufacturing impurity in dinitrotoluene. Of these compounds, 2,4-DNT was present at the highest concentration in all samples from both guns. Concentrations of 2,4-DNT varied from 982 to 175,000 $\mu\text{g/kg}$ (median value = 31,500) for surface samples collected in front of Howitzer #1 and from 1030 to 237,000 $\mu\text{g/kg}$ (median value = 40,900) in front of Howitzer #2. While these numbers appear quite large, it must be remembered that the units are $\mu\text{g/kg}$ or parts per billion, and the guns had fired about 600 rounds from the same position over several months before we sampled.

The propellant-related compounds detected at the next highest concentrations were 4A2NT and 2A4NT (Table 7). These two compounds ranged in concentration for surface soil from <d to 3,000 $\mu\text{g/kg}$ and from <d to 1,340, respectively. They were generally present in the surface soil at about two orders of magnitude lower concentration than 2,4-DNT. Concentrations of 2,6-DNT, 3,4-DNT, and 2,4,6-TNT were also found to

Table 6. Explosives concentrations in soils at 105-mm Howitzer #1 position, Fort Lewis ($\mu\text{g kg}^{-1}$).¹

Sample no.	Location ²		TNT	2,4DNT	2,6DNT	4A2NT	2A4NT	NG	2,5DNT	3,4DNT
	From muzzle (m)	Depth (cm)								
1	1.5 R		<13	8.15e3	360	631	250	299	6.7	30.1
9	3.0 R		336	1.75e5	4840	1600	666	<20	158	696
2	1.5 L		28.3	3.47e4	999	515	290	<20	23.7	123
10	3.0 L		81.6	3.18e4	211	t ⁴	t	t	14.2	122
3	0.5 C		47.1	2.89e4	1000	745	300	t	23.9	151
4	1.0 C		142	4.37e4	420	677	302	<20	25.4	175
5	1.5 C		397	1.44e5	743	1230	451	<20	71.0	503
6	2.0 C		442	1.15e5	133	3000	1340	<20	44.7	380
7	2.5 C		215	1.4e5	1314	666	372	<20	73.5	456
8	5.0 C		158	9.1e4	1330	791	272	<20	60.2	327
11	5.0 C									
	3.0 R		167	1.62e5	3840	1500	762	254	134	637
12	5.0 C		<1	982	4.8	t	t	<20	<d	<d
	3.0 L									
13	10 C		9.7	2.21e4	455	303	t	<20	20.8	108
	10C									
14	3 R		5.5	5.15e4	39.5	t	t	<20	1.9	18.1
	10C									
15	3 L		106	3.11e4	63.4	351	297	<20	10.3	107
16	2 C ⁵		85.2	6.69e4	300	<d	<d	<20	23.7	209
23	2 C	0.5-5	<1	955	16.3	t	t	<20	<d	1.78
24	2 C	5.1-9	<1	458	6.6	<d	<d	<20	<d	<d
17	2 A		125	6.19e4	1160	687	257	<20	51.0	249
18	2 B		188	9.92e4	1260	1070	398	<20	51.6	323
19	2 C		63.5	1.96e4	340	480	385	<20	16.1	88.7
20	2 D		13.6	6.27e3	7.1	300	t	<20	<d	16.5
21	2 E		20.5	2.63e4	65.8	508	t	<20	9.7	82.7
22	2 F		1.7	4.4e3	10.0	t	t	<20	<d	22.8
48	Bkg ⁶		<1	33.5	0.9	<d	<d	<20	<d	<d
	~400									

¹ Values are for surface soils except where noted. The following undetected analytes were excluded from the table: HMX, RDX, 4-aminodinitrotoluene 2-aminodinitrotoluene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, 3,5-dinitroaniline, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene,

² Locations are distances relative to the muzzle of the gun in meters; R = to the right, L = to the left, C = directly in center front. Depth in cm is also given for samples not taken from the surface.

³ Less than detection limits.

⁴ Values are trace below mean detection limits (see Table 1).

⁵ Wheel pattern of sampling: C = center of wheel; A–F clockwise around wheel circumference.

⁶ Background, soil across from Gun 1.

be at least two orders of magnitude lower than 2,4-DNT; concentrations of 2,5-DNT were generally three orders of magnitude lower than 2,4-DNT. Molecular sulfur was also detected in these soils; it is a component of the percussion primer assembly for 105-mm round.

The distribution of 2,4-DNT in the soil samples collected in front of Howitzer #1 is shown in Figure 14. All but two of these samples were collected from surface soil. Samples were collected as far as 10 m beyond the muzzle of the gun and the mean concentration of the three samples collected at 10 m was still 19,500 $\mu\text{g}/\text{kg}$.

A seven-sample set of surface soils was collected in a wheel pattern in front of Howitzer #1, 2 m from the muzzle. This was done to assess the short-range spatial

heterogeneity of analytes in the surface. The results (Fig. 14) indicate that concentrations of 2,4-DNT ranged from 4,400 to 99,200 $\mu\text{g}/\text{kg}$. Thus as found elsewhere, the distribution of munitions-related analytes is spatially very heterogeneous, even over short distances.

Only two subsurface soil samples were collected in the area in front of Howitzer #1. These samples were collected on the center line, 2 m in front of the gun, below the center samples that were collected in the wheel pattern. The concentrations of 2,4-DNT in the surface soil, in the soil segment from 0.5 to 5 cm, and from 5 cm to 9 cm were 66,900, 955, and 458 $\mu\text{g}/\text{kg}$, respectively. Thus it appears that there may be some downward migration of 2,4-DNT, but with only one set of samples, it is impossible to be certain.

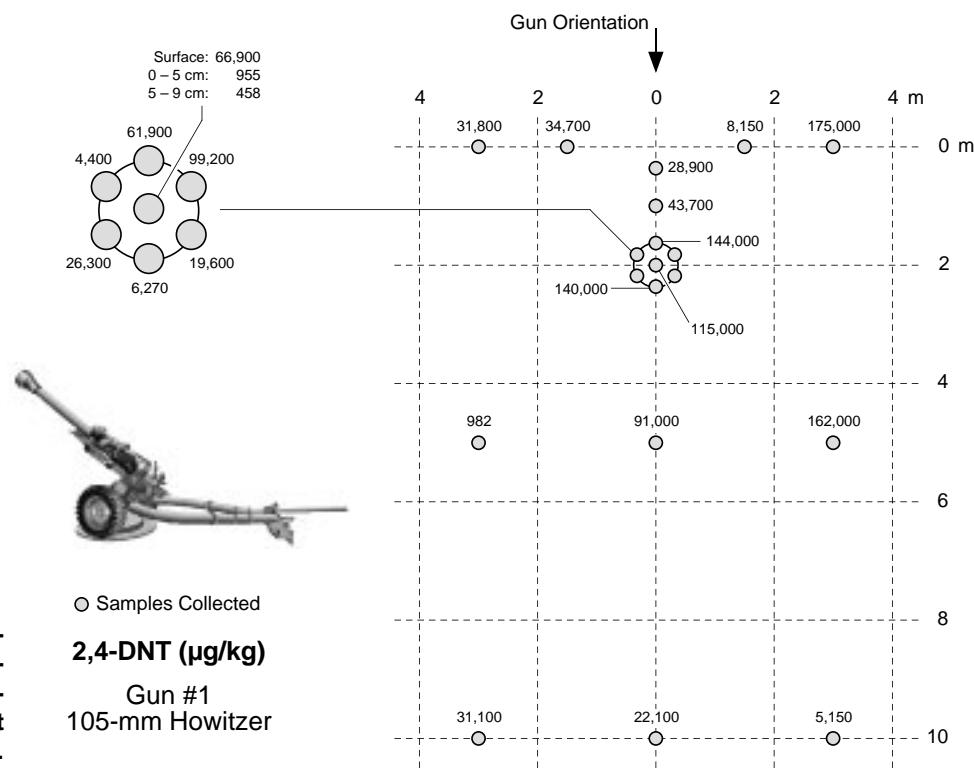
Table 7. Explosives concentrations in soils at 105-mm Howitzer #2 position, Fort Lewis ($\mu\text{g kg}^{-1}$).¹

Sample no.	Location ²	TNT	2,4DNT	2,6DNT	4ANT	2ANT	NG	2,5DNT	3,4DNT
25	1.5 R	168	9.68e4	275	1,000	334	<d ³	27.7	270
26	3.0 R	173	7.9e4	236	1,220	307	344	26.0	247
46	6.0 R	13.3	1.03e4	3.33	510	t ⁴	<d	<d	2.59
27	1.5 L	331	8.94e4	93.0	603	t	158	46.4	490
28	3.0 L	120	5.77e4	341	830	326	<d	24.0	206
47	6.0 L	206	5.84e4	108	t	t	324	23.1	288
29	0.5 C	85.2	4.09e4	132	573	t	12.0	12.4	123
30	1.0 C	77.0	3.81e4	279	502	t	<d	<d	127
31	1.5 C	71.8	4.85e4	97.5	596	t	<d	12.2	131
32	2.0 C	513	2.37e5	235	489	475	<d	67.1	732
33	2.5 C	406	1.07e5	198	1,320	602	<d	60.0	657
34	5.0 C	513	2.12e5	106	1,050	481	<d	58.3	640
35	5.0 C, 3 R	27.7	2.04e4	168	1,490	493	<d	9.0	77.0
36	5.0 C, 3 L	17.0	2.06e4	382	263	t	<d	22.2	149
37	10 C	54.1	1.6e4	8.05	497	t	84.9	4.0	44.1
38	10 C, 3 R	219	5.27e4	41.6	277	t	<d	30.2	324
39	10 C, 3 L	207	1.01e5	83.8	<d	<d	<d	26.5	296
40	15 C	82.4	3.53e4	30.3	t	t	<d	8.0	102
41	15 C, 3 R	11.1	2.45e3	22.5	<d	<d	<d	<d	16.3
42	15 C, 3 L	7.9	6.08e3	30.6	<d	<d	<d	1.8	21.5
43	20 C	<1	4.63e3	129	<d	<d	<d	3.7	19.8
44	20 C, 3 R	3.0	3.13e3	70.0	<d	<d	<d	2.8	21.0
45	20 C, 3 L	7.9	4.41e3	74.6	<d	<d	<d	3.5	23.7

¹ Values given are for surface soils except where noted. The following undetected analytes were excluded from the table: HMX, RDX, 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 1,3-dinitrobenzene, 1,3,5-trinitrotoluene, 3,5-dinitroaniline, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

² Locations are distances relative to the muzzle; R = to the right, L = to the left, C = directly in center front second; distances are from center line.

³ Less than detection limits.



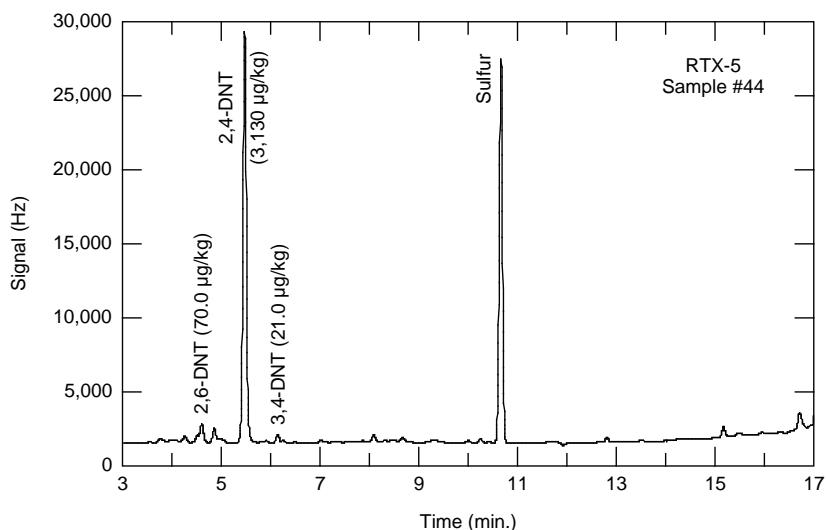
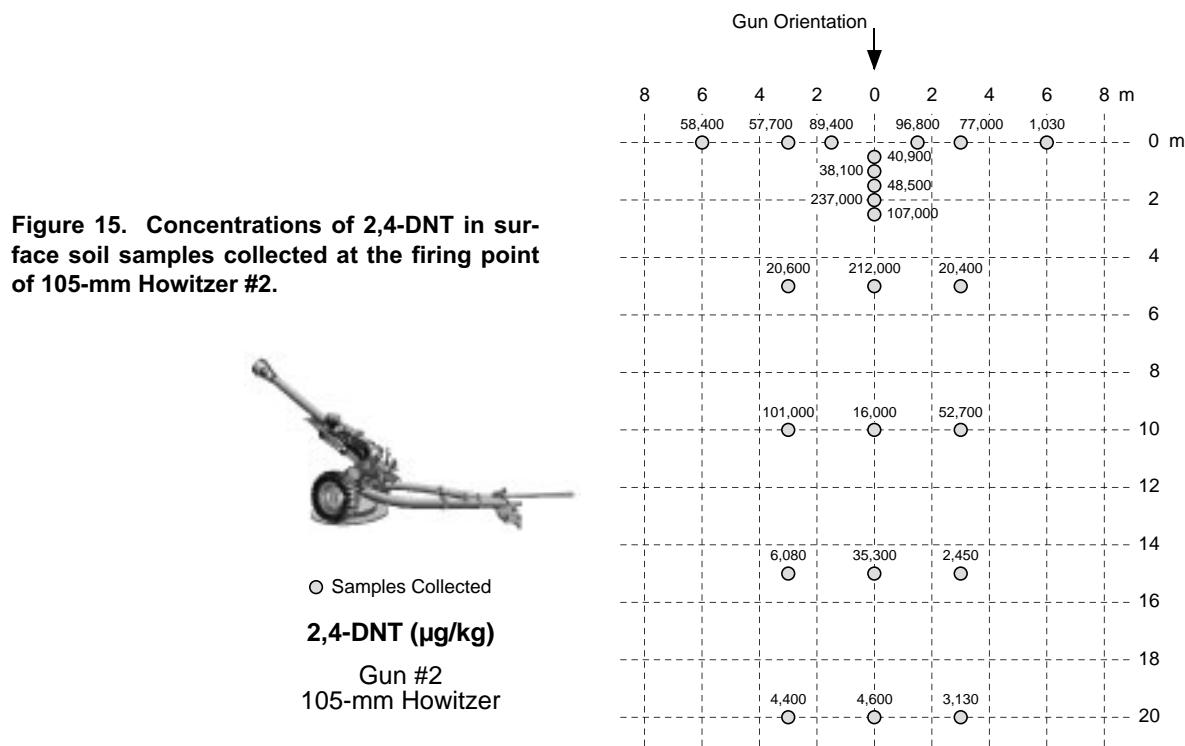


Figure 16. GC-ECD chromatogram of a soil sample collected from a 105-mm firing point at Fort Lewis.

The distribution of 2,4-DNT in the soil in front of Howitzer #2 is shown in Figure 15. Concentrations of 2,4-DNT, the two amino transformation products of 2,4-DNT, 2,4,6-TNT, and the other isomers of DNT were very similar to those found for samples collected in front of Howitzer #1. For Howitzer #2, samples were collected at distances as far as 20 m from the muzzle of the gun, on the center line and 3 m to either side of the

center line. A chromatogram for the extract of one of the samples collected 20 m from the muzzle is typical of the low level of analytical interferences found for the set of samples from the firing point extracts (Fig. 16). Even at this range, the mean concentration was found to be 4,060 µg/kg. Thus propellant residues are spread over a relatively large surface area during firing activity, but the amount of residue deposited from a

Table 8. Explosives concentrations in soils from artillery impact area, Fort Lewis ($\mu\text{g kg}^{-1}$).¹

Sample no.	Location ²	RDX	TNT	4ADNT	2ADNT	Sample no.	Location ²	RDX	TNT	4ADNT	2ADNT						
Crater A, 105-mm round < 1 week old																	
49	CR ³	<3 ⁴	<1	<1.5	<d	88	CR ³	<3	<1	<1.5	<2.5						
50	CL ³	<3	<1	<1.5	<d	89	CL ³	<3	<1	<1.5	<2.5						
51	WC	<3	<1	<1.5	<d	90	WC	<3	<1	<1.5	<2.5						
52	Wa	<3	<1	<1.5	<d	91	Wa	4.9	3.7	5.4	2.7						
53	Wb	<3	<1	<1.5	<d	92	Wb	t	6.0	20.1	10.5						
54	Wc	<3	<1	<1.5	<d	93	Wc	5.0	<1	13.2	9.0						
55	Wd	<3	<1	<1.5	<d	94	Wd	3.9	<1	11.8	2.6						
56	We	<3	<1	<1.5	<d	95	We	t	2.2	20.6	15.2						
57	Wf	<3	<1	<1.5	<d	96	Wf	t	1.3	5.6	4.5						
Crater B, 120-mm mortar, < 2 weeks old																	
62	C Ash	<3	<1	<1.5	<d	97	WC	23.7	2.9	13.1	8.8						
63	CR ³	<3	<1	6.1	2.9	98	Wa	17.3	4.0	18.5	5.8						
64	CL ³	<3	<1	6.4	2.5	99	Wb	<3	<1	<1.5	<2.5						
65	WC	<3	<1	5.9	6.4	100	Wc	19.5	t	13.7	8.8						
66	Wa	<3	<1	4.9	5.0	101	Wd	25.4	110	10.3	4.5						
67	Wb	5.8	<1	12.0	7.3	102	We	8.9	<1	<1.5	<2.5						
68	Wc	4.1	<1	12.1	6.4	103	Wf	24.9	6.4	25.5	17.0						
69	Wd	3.3	<1	7.1	3.9	Background, no crater within 3 m											
70	We	<3	<1	8.5	3.0	113	I ³	4.8	1750	140	145						
71	Wf	<3	t ⁵	8.6	5.9	114	II ³	<3	70.5	39.3	31.3						
72	Background 3 m from crater	<3	1.0	5.4	t	115	III ³	5.5	147	26.4	21.5						
73	Background 3 m from crater	<3	42.5	5.3	t	116	IV ³	<3	144	44.4	25.9						
74	Background 3 m from crater	<3	1.4	10.8	6.9	117	V ³	<3	166	39.8	19.8						
						118	VI ³	<3	59.2	13.5	5.4						
Crater C, 105-mm round, < 1 week old																	
75	E ³	<3	<1	<1.5	<d	119	C ³	<3	362	38.1	18.0						
76	E ³	<3	<1	<1.5	<d	120	C ³	<3	222	30.0	7.9						
Background, Miscellaneous ⁶																	
Crater D, 105-mm round < 1 day old																	
77	CR ³	93.4	8.7	3.9	t	58	1.5 m	<3	<1	<1.5	<2.5						
78	CL ³	81.5	<1	9.0	4.8	59	2.0 m	<3	<1	<1.5	<2.5						
79	WC	27.2	<1	<1.5	<d	60	1 m ⁷	<3	<1	<1.5	<2.5						
80	Wa	18.6	<1	3.0	2.5	61	1 m ⁸	<3	<1	<1.5	<2.5						
81	Wb	16.0	1.2	9.3	6.4	86	1.5 m	15.0	<1	14.5	14.6						
82	Wc	42.5	21.0	27.8	21.5	87	0.5 m	7.0	<1	12.1	6.6						
83	Wd	52.0	13.6	14.3	8.7	105	Burned area ⁹	20.3	<1	24.6	33.3						
84	We	20.0	1.7	7.7	5.1	106	Burned area ⁹	9.2	<1	14.1	11.3						
85	Wf	57.1	4.6	9.2	7.5												

¹ Values are for surface soils. The following undetected analytes were excluded from the table: HMX, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, 3,5-dinitroaniline, nitroglycerin, 2,5-dinitrotoluene, 3,4-dinitrotoluene, 3,5-dinitrotoluene, 2,4,5-trinitrotoluene, 2,3,4-trinitrotoluene, 3-nitroaniline.

² Location is relative to craters A through F (cross headings). CR = right of center, CL = left of center, C = center, and E = edge of crater. W = wheel pattern, C = center of wheel, a-f = clockwise around wheel circumference.

³ Composite sample.

⁴ Less than detection limit (see Table 2).

⁵ Trace detected below mean detection limit (See Table 2).

⁶ Locations in this group are distance from nearest crater.

⁷ Nearest crater assumed to be formed by an 81-mm mortar at least one year before sampling.

⁸ Nearest crater assumed to be formed by a 155-mm round at least one year before sampling.

⁹ Burn assumed to be from illumination round.

single round fired is probably quite small and perhaps not detectable even using the low-level GC-ECD method.

One surface sample was also collected about 400 m to the east of the firing position, across the road from the firing point and away from the direction of fire. Analysis of this sample indicated that 2,4-DNT was present at 33.5 µg/kg. The source of this 2,4-DNT was apparently residue that was carried downwind from the firing activity.

Artillery range impact area

Analysis of soil samples collected within the artillery range impact area is presented in Table 8. These samples were not collected randomly across the area, but were associated with specific detonation events as determined by visual observation and discussions with EOD technicians.

The first area sampled was a crater that had been caused by the impact of a 105-mm artillery round within a week of the time sampled. The type of munition that caused the crater was judged from the metal debris found within the crater and the age was estimated by the visual presence of ash. At this location, nine surface soil samples were collected and analysis indicated that no residues of explosives-related compounds were present above a detection limit of about 1 µg/kg (Table 8, samples 49–57).

The second area sampled was a crater that appeared to have been formed by the detonation of a 120-mm mortar, probably within two weeks of the date of sampling. At this location, a total of 10 samples was collected in and around the crater and three samples were collected about 3 m away from the crater (Table 8, sam-

ples 62–74). Analysis indicated that some very low levels of explosives-related residues were detectable in several of the samples associated with the crater as well as the samples collected 3 m distant. The highest concentration obtained was 42.5 µg/kg for TNT in one of the 3-m samples. Otherwise, only 4-ADNT and 2-ADNT were detected in a majority of samples, with the highest concentrations being 12.1 and 7.3 µg/kg, respectively.

The third area sampled was another 105-mm crater (Table 8, samples 75 and 76). Two composite samples were collected within the crater and no explosives-related analytes were detectable above 1 µg/kg.

The fourth area sampled was another 105-mm crater, thought to have been formed from the firing activity we observed by the National Guard the day before. Nine samples were collected near this crater; two composite samples from within the crater and a seven-sample wheel centered on the crater with the center sample taken from the bottom of the crater and the six others collected around the rim of the crater (Table 8, samples 77–85). Several different explosives-related analytes were detected in these samples, including RDX, TNT, 2,4-DNT, 4-ADNT, and 2-ADNT. A chromatogram for one of the composite samples taken from inside the crater is shown in Figure 17. RDX was found in each sample at concentrations ranging from 16.0 to 93.4 µg/kg. TNT was found in six of the nine samples at concentrations ranging from 1.2 to 21.0 µg/kg. The two transformation products of TNT (4-ADNT and 2-ADNT) were each found in eight of the nine samples at concentrations ranging from 5.4 to 20.6 µg/kg and 2.6 to 15.2 µg/kg, respectively. 2,4-DNT was detected in only two samples at concentrations of 7.3 and 9.9 µg/kg.

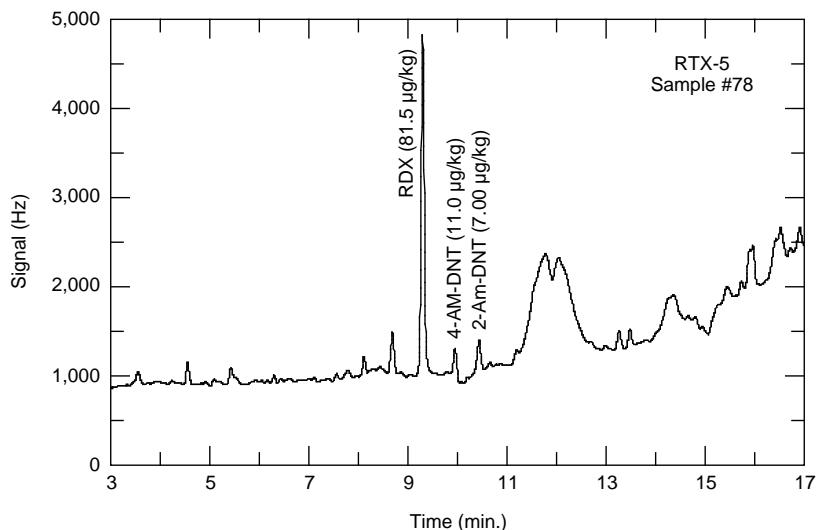


Figure 17. GC-ECD chromatogram of an extract from soil collected at a crater from the detonation of a 105-mm howitzer round.

The discovery of RDX and TNT in a number of these samples was not surprising since the 105-mm rounds contain Composition B as the main charge. The fact that 4-ADNT and 2-ADNT were found at concentrations generally as high as that of TNT was unexpected, though, since we believe that the detonation forming this crater occurred only the previous day. The rapid formation of these transformation products from TNT, however, is consistent with the half-lives observed for TNT in a recent report by Miyares and Jenkins (2000) and some earlier work by Maskarinec et al. (1991) and Grant et al. (1993).

The fifth area sampled appeared to be an old 155-mm crater that we guessed was several years old by the vegetation growing within. Again, nine samples were collected in and around this crater; two composites from within the crater and a seven-sample wheel centered on the crater as described for the previous crater sampled (Table 8, samples 88–96). No explosives-related analytes were observed for the three samples collected within the crater, but RDX, 4-ADNT, and 2-ADNT were detected in all six of the samples collected around the rim of the crater. Concentrations of RDX ranged from trace to 5.0 µg/kg, 4-ADNT ranged from 5.4 to 20.6 µg/kg, and 2-ADNT ranged from 2.6 to 15.2 µg/kg. TNT was also detected in four of the six samples with concentrations ranging from 1.3 to 6.0 µg/kg; 2,4-DNT was observed in two samples at 6.9 and 15.3 µg/kg. While detectable, all of these residues are present at very low concentrations and wouldn't have been detectable using SW-846 Method 8330. In addition, the main charge for 155-mm rounds generally contains TNT, not Composition B, and the RDX found in these samples appears to have originated from a source other than a 155-mm detonation.

The sixth area of samples was a series of background samples collected in a wheel pattern within the range, but not close to any visual crater (Table 8, samples 97 to 103). Low levels of RDX, 4-ADNT, 2-ADNT, and TNT were observed in these samples, but concentrations were always below 30 µg/kg. These results indicate that low concentrations of explosives residues are distributed in some places over fairly large areas even when no craters are observable, but it is impossible to identify a specific source.

Next we sampled a series of six craters that were identified by our EOD team as recent 105-mm craters, probably formed from detonations within a week of sample collection (Table 8, samples 113–118). Composite samples from the inside walls of all six of these craters were similar in that TNT, 4-ADNT, and 2-ADNT were the residues at highest concentration in each case. TNT concentrations ranged from 59.2 to 1750 µg/kg in these samples; concentrations of 4-ADNT and 2-ADNT

ranged from 13.5 to 140 µg/kg and 5.4 to 145 µg/kg, respectively. RDX was observed in only two of these samples and the concentrations were low, 4.8 and 5.5 µg/kg. Since the 105-mm rounds contain Composition B as the main charge, either RDX has preferentially leached out of these craters, or the residues we find here were deposited from a TNT-containing round instead and were not associated with the 105-mm rounds that made these craters. The preferential leaching of RDX from these recent craters would be somewhat surprising since it is thought to dissolve slower than TNT from solid Composition B. On the other hand, once dissolved, soils have much less tendency to sorb RDX than TNT and so it is possible that this is the explanation for the minimal presence of RDX in these samples.

The eighth area sampled was a crater formed by the detonation of a 60-mm mortar round that was estimated to be about a year old (Table 8, samples 119–120). Two composite samples were collected from within the crater and TNT, 4-ADNT, and 2-ADNT were found in both. Concentrations of 222 and 362 µg/kg were found for TNT, 30.0, and 38.1 for 4-ADNT, and 7.9 and 18.0 for 2-ADNT. Since the main charge in 60-mm mortar rounds is 0.43 kg of Composition B, it is surprising that we did not find RDX in this crater if these residues were indeed due to the detonation of a 60-mm round. Perhaps the residues we observed in these samples actually originated from a TNT-containing round such as a 155-mm artillery round instead, or RDX had leached from this crater during the year since the detonation had occurred.

The next series of samples was collected at various points throughout the range. These samples were taken from various areas as described in Table 8 (samples 58–61, 86–87, and 105–106). Samples 58 and 59 were taken a short distance from an unidentified crater and contained no measurable residue. Likewise, samples 60 and 61 were taken near two very old craters and no residues were detectable here either. Samples 86 and 87 were collected next to more recent craters and low concentrations of RDX, 4-ADNT, and 2-ADNT were found in each. Finally, samples 105 and 106 were taken from an area that had recently burned because of an illumination round, and again concentrations of RDX, 4-ADNT, and 2-ADNT were detectable.

The final samples collected from the artillery impact area were samples associated with a 155-mm round that had undergone a low-order detonation (Table 9). This round was broken open and was still filled with the unexploded main charge (Figure 18). This material was sampled and the analysis indicated that it was 99.96% 2,4,6-TNT with a small percentage of the manufacturing impurity, 2,4-DNT (0.04%). Concentrations of 2,4,6-TNT and its associated impurities and environ-

Table 9. Explosives concentrations in proximity to a single low-order detonation of a 155-mm round on the artillery range at Fort Lewis ($\mu\text{g kg}^{-1}$ except where noted).¹

Sample no.	Location ²	TNT	2,4DNT	2,6DNT	4ADNT	2ADNT	1,3-DNB	1,3,5TNB	2,5DNT
104	Residue ³	99.96%	0.04%	<d ⁴	<d	<d	<d	<d	<d
107	Surface	1.51e7	4.01e4	<d	1.1e5	1.02e5	1.21e3	1.47e4	<d
111	5 cm ⁵	7.1e5	1.e4	264	1.46e5	1.53e5	281	<d	368
112	10 cm ⁵	4.63e4	1.96e4	41.2	2.e4	2.97e4	37.4	141	25.9
108	15 cm ⁵ W ⁶	2.5e3	9.4	<d	194	188	<d	62.5	<d
109	15 cm ⁵ E	886	52.7	6.1	3.e3	3.38e3	<d	66.0	<d
110	15 cm ⁵ S	1.5e4	221	7.7	7.23e3	7.69e3	10.4	382	<d

¹ Values are for surface soils except where noted. The following undetected analytes were excluded from the table: HMX, RDX, nitroglycerin, 2,5-dinitrotoluene, 3,4-dinitrotoluene. The following analytes were excluded from the table, but were detected in sample 111 (concentrations are given in parentheses): 2,4,5-trinitrotoluene (69.0), and 2,3,4-trinitrotoluene (17.9). The following analytes were excluded from the table, but were detected in sample 112, 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene, 3,5-dinitroaniline, 3,5-dinitrotoluene, 3-nitroaniline.

² Locations are relative to the low-order round.

³ High-explosive residue remaining in the low-order shell.

⁴ Less than detection limits.

⁵ Depth beneath the round.

⁶ Direction from the round. W = west, E = east, S = south.



Figure 18. Sampling a 155-mm round that was broken open by a low-order detonation.

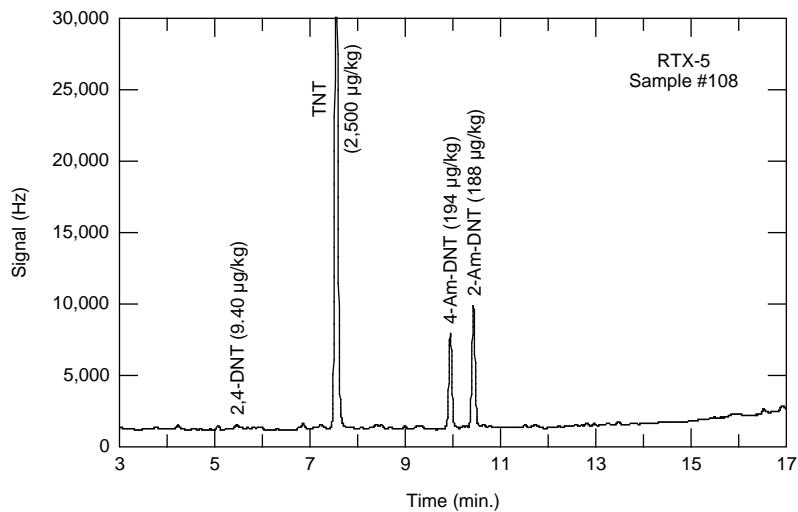


Figure 19. Chromatogram of soil collected 15 cm west of a 155-mm round that was broken open by a low-order detonation.

mental transformation products were found at very high concentrations in soils collected next to this round and at depth, under the round. A chromatogram for the extract of a sample collected 15 cm west of the round is shown in Figure 19.

For example, surface soil collected directly under the round had a 2,4,6-TNT concentration of 15,100,000 µg/kg or 1.5%. This was four orders of magnitude higher than any samples collected next to craters formed from high-order detonations. This sample also contained high concentrations of 4-ADNT and 2-ADNT, 110,000 and 102,000 µg/kg, respectively, moderately high concentrations of 2,4-DNT and 1,3,5-TNT, and detectable concentrations of other isomers of DNT and 1,3-DNB.

Samples of soil collected at depths of 5 cm and 10 cm below this round also had very high 2,4,6-TNT concentrations, 710,000 and 46,300 µg/kg, respectively, and the 5-cm sample had even higher concentrations of 4-ADNT and 2-ADNT than the surface soil. Concentrations of 2,4,6-TNT and 4-ADNT and 2-ADNT, in particular, are still moderately high in the soils collected at a distance of 15 cm on three sides of this low-order round. These results indicate what a high concentration contamination source is caused by a low-order detonation. Clearly concentrations are many orders of magnitude greater than those from rounds that detonate as engineered.

Water analyses

The results for the analysis of water samples from monitoring wells and seeps at Fort Lewis are presented in Table 10. These analyses were conducted using GC-ECD method 8095 at CRREL and RP-HPLC-UV method 8330 at ERDC-EL and at the contract laboratory. Only RDX was detected above analytical detection limits. The agreement among the three data sets is excellent, even though two different methods were used and the concentrations are near the detection limit of the HPLC method.

Overall, RDX was detected in eight of the ten water samples from Fort Lewis. These results confirm that

Table 10. RDX concentrations in ground-water and surface water seepages around the perimeter of the artillery range at Fort Lewis (µg/L).¹

Sample no.	CRREL ²	EL ³	Anteon Corporation ³
MW1	0.28	0.38	0.3
MW2	0.19	0.27	0.2
MW3	0.18	na ⁴	0.2
MW4	0.51	0.59	0.5
MW7	<0.1 ⁵	na	<0.2
A1ASP01	0.31	na	0.4
A1ASP02	0.15	na	0.2
A1ASP03	0.26	na	0.3
A1ASP04	0.73	na	0.8
A1ASP05	<0.1	na	<0.2

¹ Samples were collected in August 2000. RDX was the only analyte detected.

² Analyzed by Method 8095, GC-ECD (U.S. EPA 1998).

³ Analyzed by Method 8330, RP-HPLC-UV (U.S. EPA 1994).

⁴ Sample not analyzed by this laboratory.

⁵ Less than detection limits.

there is a low level of RDX contamination in the aquifer below the impact ranges at Fort Lewis. The concentrations of RDX in these water samples are below 1 µg/L in all cases, though; 2 µg/L is the continuous lifetime human health advisory level for RDX (EPA 1988).

Geochemical parameters

Groundwater geochemistry is typical of the geographic area (Table 11). Groundwater is generally soft (sum of calcium and magnesium less than 50 mg L⁻¹). One sample, MW07, slightly exceeds the drinking water standard for total iron (0.3 mg L⁻¹). None of the samples exceed the drinking water standard for manganese (0.05 mg L⁻¹). Nitrate/nitrite values are well within the range for natural waters (0.1 to 10 mg L⁻¹). Total organic carbon, sulfate, and chloride values are relatively low, not atypical for this environment.

Table 11. Geochemical parameters in groundwater at Fort Lewis (mg L⁻¹).

Well	Calcium	Iron	Manganese	Magnesium	Nitrate/Nitrite	TOC ¹	Sulfate	Chloride
MW01 ²	8.60	0.069	0.007	2.96	0.37	<3.0 ³	13J ⁴	2.0J
MW02	9.47	<0.02	<0.001	3.63	0.23	<3.0	6.4J	2.1J
MW03	7.87	0.048	0.002	3.05	0.26	<3.0	<20	1.7J
MW04	7.70	<0.02	<0.001	2.67	0.35	<3.0	<20	2.0J
MW07	11.5	0.319	0.014	4.86	1.6	<3.0	<20	1.6J
A1ASP03 ⁵	7.10	0.029	0.004	2.45	0.055J	<3.0	<20	1.6J
A1ASP05	7.66	<0.02	<0.001	2.31	0.44	<3.0	<20	2.2J

¹ Total organic carbon.

² Monitoring well number.

³ Less than detection limit.

⁴ J values are below the statistically reliable detection limit.

⁵ Seepage area number.

Historical firing records

Firing records for the six most heavily used rounds indicated that the 105-mm artillery round was the item most heavily fired, followed by the 81-mm mortar and the 155-mm artillery round (Table 12). Estimates of range loading of explosives residues from each type of round can be made by making several assumptions and using known low-order detonation rates (Table 13). For example, firing records indicate that 7458 105-mm howitzer rounds were fired into the Fort Lewis impact area in 2000 (Table 12). On average, about 0.07 percent of those fired undergo a low-order detonation (Table 13). Thus, for 2000, we estimate that five of these 105-mm rounds would have undergone a low-order detonation. If we assume that all the 105-mm rounds contained Composition B as the main charge, then each round would contain about 1252 g of RDX. If half of the main charge remained undetonated for each low-order detonation, then 3130 g of RDX would be deposited on the Fort Lewis range from low-order detonations of 105-mm howitzer rounds in 2000.

We can estimate the amount of residue deposited from high-order detonations as well. For the total number of 105-mm rounds fired in 2000, we estimate that 327 were duds and five rounds were low-order detonations (Table 13). Thus, about 7126 rounds underwent high-order detonations. At this point, there is no experimentally derived estimate of the amount of explosives residue that is produced from the detonation of a 105-mm round; however, there are estimates for 60-mm mortars that also contain Composition B. Each 60-mm round has 258 g of RDX or about 20.6% of the RDX present in the 105-mm round. Experiments conducted by firing 60-mm rounds onto a snow-covered range indicate that about 0.00007% of the RDX originally present in the round remains undetonated and is deposited on the range (Jenkins et al. 2000). If we assume that this same percentage would apply to high-order detonations of 105-mm rounds, then each detonation would deposit about 0.88 mg of RDX. Multiplying this by the 7126 high-order detonations results in an estimate of about 6.2 g of RDX deposited in 2000.

It is important to remember that these are preliminary estimates and source terms for rounds other than 60-mm mortars are being developed from additional detonation experiments. However, it appears that even a small number of low-order detonations contribute a very large percentage of the total explosives residues deposited. If the 0.00007% figure is correct, then one low-order detonation in which half of the explosive is not destroyed contributes as much residue as about 700,000 high-order detonations. Based on these esti-

Table 12. Firing record for 1997–2000 at Fort Lewis.¹

Round	DODIC ²	1997	1998	1999	2000 ³	Total
81-mm	C256	1,997	2,112	2,789	2,075	8,973
105-mm	C445	10,585	3,166	9,505	7,458	30,714
120-mm	C623	474	— ⁴	—	359	833
120-mm	C788	—	75	288	—	363
107-mm	C697	219	128	262	216	825
155-mm	D544	207	7,564	261	841	8,873

¹ Records encompass the available electronic database from January 1997 through July 2000 and include the most commonly fired items as indicated by Del Larson, Range Operations Officer.

² Department of Defense Identification Code.

³ Data through July 2000 only.

⁴ No record of firing for this item in this year.

Table 13. Mean dud and low-order detonation rates for munitions items commonly used at Fort Lewis.¹

Round	DODIC ²	Items tested	Duds (%)	Low orders (%)
81-mm	C256	9,122	2.16	0.22
105-mm	C445	10,003	4.39	0.07
120-mm	C623, C788	— ³	—	—
107-mm (4.2-in.) ²	C697	1,518	2.24	0.02
155-mm	D544	6,216	2.75	0.02

¹ Rates based on test data acquired by U.S. Army Defense Ammunition Center, McAlester, Oklahoma (Dauphin and Doyle 2000).

² Department of Defense Identification Code.

³ No data.

mates, efforts should be made to locate and remove the debris from low-order detonations as soon as possible. This action alone may substantially reduce the amounts of explosives residues contaminating surface soils at impact ranges.

SUMMARY AND CONCLUSIONS

Three training areas were sampled at Fort Lewis, Washington: an impact area within the hand grenade range, a 105-mm howitzer firing point, and a portion of the impact area within the heavy artillery and mortar range. A set of eleven water samples also was analyzed from monitoring wells and seeps that are adjacent to the artillery impact area. Soil samples were also collected at a hand grenade range at Fort Richardson, Alaska.

With respect to the two hand grenade ranges, RDX was detected in all of the 96 soil samples collected, both surface and shallow subsurface. The median and maximum concentrations of RDX in surface soils at these sites were 1560 µg/kg and 51,200 µg/kg at Fort Lewis, and 28.9 µg/kg and 518 µg/kg at Fort Richardson. TNT and HMX concentrations were also detectable in most soils from these two grenade ranges.

Overall, concentrations of explosives-related con-

taminants were an order of magnitude higher at the Fort Lewis grenade range than at the Fort Richardson range, probably due to a higher usage at Fort Lewis. Although RDX concentrations were moderate at these ranges, the size of these ranges is small compared with other training ranges, and remediation seems doable if judged to be of sufficient concern with respect to groundwater contamination.

At the Fort Lewis artillery range, surface and near-surface soil samples were collected at a 105-mm howitzer firing point and at the main impact area. At the firing point, samples were collected in front of two howitzers that had each fired about 600 rounds in the same position. Samples were collected at distances out to 10 m and 20 m for the two guns. Overall, 2,4-DNT, a component of single-based propellant, was found at concentrations as high as 237,000 µg/kg in surface soil. Whether 2,4-DNT is leaching deep into the profile is uncertain because only two shallow subsurface samples were collected.

In the artillery range impact area, soil samples were collected in and around craters formed by detonation of various artillery and mortar rounds. Concentrations of explosives residues associated with these high-order detonations were very low, often below a detection limit of 1 µg/kg (1 part per billion). RDX, the analyte of most concern for groundwater contamination, was always less than 100 µg/kg in these soil samples

Soil samples were also collected under and adjacent to a 155-mm round that had undergone a low-order detonation. In this case, the concentration of TNT was extremely high in the surface soil under the round (1.5%) and was still substantial in soils collected at 5- and 10-cm depths. Clearly the residues of explosives resulting from low-order detonations are many orders of magnitude higher than those that result from high-order detonations and efforts should be made to locate and eliminate the resulting debris from low-order detonations.

Results of analysis of water samples obtained from five monitoring wells and five seeps that border the artillery range at Fort Lewis indicated a low level (<1 µg/L) of RDX contamination. The source of this contamination was not determined. Results of soil analyses from Fort Lewis and Fort Richardson indicate that very low concentrations of explosives residues are more widespread at testing and training ranges than observed previously. The use of an analytical method that has lower detection limits than the current standard method for explosives residues, SW-846 Method 8330 (U.S. EPA 1994), detection limit of 250 µg/kg, allowed delineation of contamination at training ranges. The GC-ECD method developed recently by Walsh and Ranney (1998) has detection limits near 1 µg/kg for many explosives residues and is particularly appropriate for use in

range characterization studies. Method 8330 was adequate for characterization of explosives contamination of army ammunition plants and depots, where concentrations were much higher, but these limits are inadequate to delineate contamination at training ranges.

The distribution of explosives residues at all the ranges investigated was spatially very heterogeneous. For soils at hand grenade ranges, concentrations of explosives-related compounds differed by over two orders of magnitude for soil samples collected less than a meter apart. At artillery firing points, concentrations of propellant residues differed by as much as an order of magnitude over the same distance. At artillery impact areas, the spatial heterogeneity was large as well, although it is difficult to define numerically since many of the concentrations were below detection limits. Concentrations of explosives residues for soils collected in areas that were visibly free of craters, however, often had explosives concentrations as high or higher than soils collected from the rim of a fresh crater. Thus thought must be given to sampling methods such as compositing in order to provide representative samples for a given area.

From preliminary estimates of residues produced from high-order detonations and the frequency of low-order detonations, it appears that low-order detonations produce a large portion of the residues deposited on surface soils in artillery impact areas. Continued work is underway to provide better estimates of the amount of residues produced from detonations of various military munitions and these experiments will provide better estimates in the future.

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14. ABSTRACT (cont'd)

Soil samples were also collected from a number of areas around detonation craters formed by 105-mm and 155-mm howitzers, and 60-, 81- and 120-mm mortars. Concentrations of explosives residues in and around these craters were generally barely detectable, indicating that only minor amounts of explosives residue are deposited during high-order detonations of army munitions.

Soil samples were also collected below and adjacent to a 155-mm howitzer shell that had undergone a low-order detonation. These samples were heavily contaminated with TNT and its environmental transformation products. These results indicate that efforts should be made to find and remove the resulting debris from low-order detonations whenever possible to prevent leaching of contaminants to groundwater.

Water samples collected from five groundwater monitoring wells and five seeps around the artillery impact areas at Fort Lewis were also analyzed for explosives; 8 of the 10 were found to contain very low (<1.0 µg/L) concentrations of RDX. The source of this RDX is unknown.